Development of a New Lewis Acid-Catalyzed [3,3]-Sigmatropic Rearrangement: The Allenoate-Claisen Rearrangement

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Supporting Information

General Information. All reactions were performed using oven-dried glassware under an atmosphere of dry argon. Non-aqueous reagents were transferred under argon by syringe. Organic solutions were concentrated under reduced pressure using a Buchi rotary evaporator. Methylene chloride was distilled from CaH_2 or filtered through a column charged with Al_2O_3 (solvent purification system) immediately prior to use. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl immediately prior to use. Acid chlorides were distilled immediately prior to use. Allenic esters were prepared according to the procedure of Lang and Hansen.[1] All other commercial reagents were used as provided. Air sensitive solids were dispensed in an inert atmosphere glovebox. Chromatographic purification of products was accomplished using forced-flow chromatography on ICN 60 32-64 mesh silica gel 63 according to the method of Still.[2] Thin-layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica gel 60-F plates. Visualization of the developed chromatogram was performed by fluorescence quenching, or $KMnO_4$ or p-anisaldehyde stain.

^1H and ^{13}C NMR were recorded on Mercury 300 (300 MHz and 75 MHz) as noted, and are internally referenced to residual protio solvent signals. Data for ^1H NMR

[1] Lang, R. W.; Hansen, H.-J. *Org. Syn* **1984**, *62*, 202.
[2] Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* **1978**, *43*, 2923.

are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported in terms of chemical shift. IR spectra were recorded on a Perkin-Elmer 1600 Series spectrometer using NaCl salt plates, and reported in terms of frequency of absorption (cm^{-1}). Mass spectra were obtained from the UC Irvine Mass Spectral Facility. Gas chromatography was performed on Hewlett-Packard 6890 Series gas chromatograph equipped with split-mode capillary injection system and flame ionization detector using a C&C Column Technologies CC-1701 (30 m x 0.25 mm).

General Procedure A: The allylic amine and the allenic ester in CH_2Cl_2 were added sequentially to a 2 dram vial containing $Zn(OTf)_2$. The resulting solution was stirred until the allenic ester was completely consumed (0.25-24 h) as determined by TLC (20% EtOAc:hexanes). The solution was diluted with an equal volume of Et_2O and flushed through a short (8 x 30 mm) silica gel plug with an additional equal volume of Et_2O. The combined filtrates were concentrated and the resulting crude residue was purified by silica gel chromatography to afford the title compounds.

General Procedure B: The β-amino-α,β-unsaturated ester was taken up in 5% EtOAc:hexanes and silica gel was added. The resulting slurry was stirred until the starting material was completely consumed as determined by TLC (10% EtOAc:hexanes, p-anisaldehyde stain.) The slurry was filtered through a cotton plug and the silica gel was

flushed with ether. The combined filtrates were concentrated to afford the pure β-keto esters products.

General Procedure C: The β-amino-α,β-unsaturated esters were hydrodeaminated according to the procedure of Brown.[3] The β-amino-α,β-unsaturated ester (0.1 mmol) in THF (0.25 mL) was added to 9-BBN in a 2-dram vial, and the solution was stirred for 3h. Solvent was removed in vacuo and MeOH (0.5 mL) was added. The vial was heated briefly with a heat gun and then left at room temperature for 0.5h. Solvent was removed in vacuo and the resulting residue was dissolved in pentane (2 mL), washed with 1N HCl (0.5 mL) and H_2O (0.5 mL), dried (Na_2SO_4) and concentrated. The resulting residue was purified by silica gel chromatography to provide the α,β-unsaturated ester product.

General Procedure D: To the β-amino-α,β-unsaturated ester (0.2 mmol) in MeOH (3 mL) was added $NaCNBH_3$ (0.2 g, 3.2 mmol) followed by trifluoroacetic acid (0.3 mL). After 0.5 h the solution was basified to pH 12 with 1N NaOH, extracted with Et_2O (3 x 1 mL), dried (Na_2SO_4) and concentrated. The crude residue was taken up in THF (1 mL) and mCPBA (0.2 g, 1.2 mmol) was added. After 15 min the solution was diluted with Et_2O (2 mL) and washed with H_2O (3 x 1 mL), 20% $Na_2S_2O_3$ (1 mL), and 1N NaOH (2 mL), dried (Na_2SO_4) and concentrated. The crude residue was purified by silica gel chromatography to provide the α,β-unsaturated ester product.

[3] Singaram, B.; Rangaishenvi, M. V.; Brown, H. C.; Goralski, C. T.; Hasha, D. L. *J. Org. Chem.* **1991**, *56*, 1543.

Benzyl (*E*)-4,6-Dimethyl-3-pyrrolidinohepta-2,6-dienoate: Prepared according to general procedure A from methallyl pyrrolidine (144 mg, 1.14 mmol), benzyl penta-2,3-dienoate (108 mg, 0.58 mmol), and $Zn(OTf)_2$ (20 mg, 0.06 mmol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.39 (m, 5H, Ar**H**), 5.08 (s, 2H, C**H**$_2$Ph), 4.73 (d, *J* = 1.5 Hz, 1H, C**H**$_2$=C), 4.71 (s, 1H, C**H**$_2$=C), 4.48 (s, 1H, NC=C**H**), 3.34 (brs, 4H, N(C**H**$_2$CH$_2$)$_2$), 2.83 (brs, 1H, C**H**CH$_3$), 2.31 (brm, 2H, C(CH$_3$)C**H**$_2$), 1.88 (m, 4H, N(CH$_2$C**H**$_2$)$_2$), 1.77 (s, 3H, CH$_2$=CC**H**$_3$), 1.21 (brs, 3H, CHC**H**$_3$); LRMS (CI) *m/z* 313 $(M)^+$; HRMS (CI) exact mass calc d for ($C_{20}H_{27}NO_2$) requires *m/z* 313.2042, found *m/z* 313.2037.

The yield was determined by enamine hydrolysis according to procedure B using 2 mL solvent and 0.8 g silica gel to provide the β-keto ester as a colorless oil in 80% yield (120 mg, 0.46 mmol). IR (thin film) 3072, 3034, 2972, 2936, 1746, 1714, 1649, 1623, 1456, 1376, 1310, 1262, 1225, 1154 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.36 (m, 5H, Ar**H**), 5.17 (s, 2, C**H**$_2$Ph), 4.78 (s, 1H C**H**$_2$=C), 4.68 (s, 1H C**H**$_2$=C), 3.54 (s, 2H, C(O)C**H**$_2$), 2.82 (dq, *J* = 7.2, 14.4, 1H, CH$_3$C**H**), 2.39 (dd, *J* = 6.0, 14.1 Hz, 1H, C(CH$_3$)C**H**$_2$), 2.00 (dd, *J* = 8.3, 14.3 Hz, 1H, C(CH$_3$)C**H**$_2$), 1.68 (s, 3H, CH$_2$=CC**H**$_3$), 1.08 (d, 3H, *J* = 7.2 Hz, CHC**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.8, 167.2, 142.5, 135.6, 128.8, 128.6, 128.5, 113.1, 67.3, 48.1, 44.8, 41.0, 22.5, 16.2; LRMS (CI) *m/z* 261 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{16}H_{21}O_3$) requires *m/z* 261.1490, found *m/z* 261.1500.

Benzyl (2*E*,4*R,5*S**)-4-Methyl-5-phenyl-3-pyrrolidinohepta-2,6-dienoate:** Prepared according to general procedure A from cinnamyl pyrrolidine (216 mg, 1.15 mmol), benzyl penta-2,3-dienoate (108 mg, 0.57 mmol), and $Zn(OTf)_2$ (20 mg, 0.06 mmol). The

crude residue was purified by silica gel chromatography (10% EtOAc:hexanes) to afford the title compound as a light yellow oil in 97% yield (208 mg, 0.55 mmol), 94:6 *syn:anti*, 3:1 *E:Z*. *Syn, E* isomer: IR (thin film) 3062, 3029, 2972, 2873, 1676, 1560, 1455, 1400, 1345, 1128 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.29-7.43 (m, 10H, Ar**H**), 6.07 (ddd, *J* = 9.8, 9.8, 17.1, 1H, CH_2=C**H**), 5.44 (dq, *J* = 7.7, 11.6, 1H, C**H**CH_3), 5.19 (d, *J* = 12.6 Hz, 1H, C**H**$_2$Ph), 5.12 (d, *J* = 12.6 Hz, 1H, C**H**$_2$Ph), 4.90 (d, *J* = 7.8 Hz, 1H, C**H**$_2$=CH), 4.85 (s, 1H, C**H**$_2$=CH), 4.59 (s, 1H, NC=C**H**), 3.39-3.48 (m, 4H, N(C**H**$_2$$CH_2$)$_2$), 1.88-1.93 (m, 4H, N($CH_2$C**H**$_2$)$_2$), 1.01 (d, 3H, C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 167.3, 166.9, 165.4, 143.7, 141.5, 141.1, 138.0, 129.0, 128.8, 128.7, 128.6, 128.6, 128.3, 128.2, 128.1, 127.8, 127.7, 126.7, 126.5, 115.7, 114.0, 85.9, 84.1, 64.8, 64.7, 55.2, 51.1, 50.0, 49.6, 43.5, 37.1, 25.7, 25.6, 16.4, 15.1; LRMS (CI) *m/z* 375 $(M)^+$; HRMS (CI) exact mass calc d for ($C_{25}H_{29}NO_2$) requires *m/z* 375.2198, found *m/z* 375.2199.

The diastereomer ratio was determined by derivitization of the product to benzyl (2*E*,4*R**,5*R**)-4-methyl-5-phenylhepta-2,6-dienoate according to general procedure C and analysis by ^1H NMR. ^1H NMR (300 MHz, $CDCl_3$) δ 7.15-7.39 (m, 10H, Ar**H**), 7.00 (dd, *J* = 8.2, 15.4 Hz, 1H, C**H**=$CHCO_2$), 5.90-6.01 (m, 1H, CH_2=C**H**), 5.86 (d, *J* = 15.4 Hz, 1H, CH=C**H**CO_2), 5.19 (s, 2H, C**H**$_2$Ph), 5.10 (d, *J* = 9.9 Hz, 1H, C**H**$_2$=CH), 5.01 (d, *J* = 17.6 Hz, 1H, C**H**$_2$=CH), 3.17 (dd, *J* = 8.2, 8.5 Hz, 1H, PhC**H**), 2.69 (dd, *J* = 6.6, 8.5 Hz, 1H, C**H**CH_3), 0.93 (d, *J* = 6.6 Hz, 3H, C**H**$_3$); LRMS (CI) *m/z* 307.2 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{21}H_{23}O_2$) requires *m/z* 307.1698, found *m/z* 307.1695.

Benzyl (2*E*,4*R,5*S**)-4,5-Dimethyl-3-pyrrolidinohepta-2,6-dienoate:** Prepared according to general procedure A from (*E*)-crotyl pyrrolidine (144 mg, 1.14 mmol),

benzyl penta-2,3-dienoate (108 mg, 0.58 mmol), and $Zn(OTf)_2$ (20 mg, 0.06 mmol) to provide the crude enamine, >98:2 *syn:anti*. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24-7.39 (m, 5H, Ar**H**), 5.67-5.76 (m, 1H, CH_2=C**H**), 5.11 (d, *J* = 12.9 Hz, 1H, C**H**$_2$Ph), 5.08 (d, *J* = 13.2 Hz, 1H, C**H**$_2$Ph), 4.74-4.94 (m, 3H, C**H**$_2$=CH and CC**H**CH_3), 4.47 (s, 1H, NC=C**H**), 3.31 (brs, 4H, N(C**H**$_2CH_2)_2$), 2.35 (m, 1H, CH_2=CHC**H**), 1.84 (brs, 4H, N(CH_2C**H**$_2)_2$), 1.22 (brs, 3H, CCHC**H**$_3$), 1.12 (d, *J* = 5.4 Hz, 3H, CH_2=CHCHC**H**$_3$); LRMS (CI) *m/z* 313 $(M)^+$; HRMS (CI) exact mass calc d for ($C_{20}H_{27}NO_2$) requires *m/z* 313.2042, found *m/z* 313.2044.

The yield was determined by enamine hydrolysis according to procedure B using 3 mL solvent and 1.5 g silica gel to provide the beta keto ester as a colorless oil in 95% yield (142 mg, 0.55 mmol). IR (thin film) 3068, 3034, 2974, 1746, 1713, 1641, 1456, 1419, 1377, 1307, 1222, 1152 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.36 (m, 5H, Ar**H**), 5.71 (ddd, *J* = 7.1, 10.6, 16.9 Hz, 1H, CH_2=C**H**), 5.16 (s, 2H, C**H**$_2$Ph), 4.97-5.05 (m, 2H, C**H**$_2$=CH), 3.51 (s, 2H, C(O)C**H**$_2$), 2.44-2.65 (m, 2H, CH_2=CHC**H** and CC**H**CH_3), 1.04 (d, *J* = 7.1 Hz, 3H, CCHC**H**$_3$), 0.96 (d, *J* = 7.1 Hz, 3H, CH_2=CHCHC**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.7, 167.2, 141.5, 135.6, 128.8, 128.6, 128.5, 115.0, 67.3, 51.7, 49.0, 39.7, 16.0, 12.8; LRMS (CI) *m/z* 261 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{16}H_{21}O_3$) requires *m/z* 261.1493, found *m/z* 261.1490.

The diastereomer ratio was determined by derivitization of the product to benzyl (2*E*,4*R**,5*R**)-4,5-dimethylhepta-2,6-dienoate according to general procedure C and analysis by ^{1}H NMR. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.39 (m, 5H, Ar**H**), 6.98 (dd, *J* = 7.8, 15.9 Hz, 1H, C**H**=$CHCO_2$), 5.84 (dd, *J* = 1.2, 15.9 Hz, 1H, CH=C**H**CO_2), 5.64-5.76 (m, 1H, CH_2=C**H**), 5.18 (s, 2H, C**H**$_2$Ph), 5.03 (s, 1H, C**H**$_2$=CH), 4.97-5.03 (m, 1H,

C**H**$_2$=CH), 2.18-2.37 (m, 2H, 2CH$_3$C**H**), 1.07 (d, *J* = 6.6 Hz, 3H, C**H**$_3$), 0.99 (d, *J* = 7.2 Hz, 3H, C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 153.4, 141.4, 136.3, 128.7, 128.4, 128.4, 120.6, 114.9, 66.4, 42.7, 41.8, 17.2, 16.5; LRMS (CI) *m/z* 244.2 $(M)^+$; HRMS (CI) exact mass calc d for ($C_{16}H_{20}O_2$) requires *m/z* 244.1463, found *m/z* 244.1469.

Benzyl (2E,4*R,5*R**)-4,5-Dimethyl-3-pyrrolidinohepta-2,6-dienoate:** Prepared according to general procedure A from (*Z*)-crotyl pyrrolidine (144 mg, 1.14 mmol), benzyl penta-2,3-dienoate (108 mg, 0.58 mmol), and $Zn(OTf)_2$ (20 mg, 0.06 mmol) to provide the crude enamine, <2:98 *syn:anti*. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25-7.39 (m, 5H, Ar**H**), 5.63-5.78 (m, 1H, CH_2=C**H**), 4.97-5.14 (m, 4H, C**H**$_2$Ph and C**H**$_2$=CH), 4.55 (s, 1H, NC=C**H**), 3.33-3.37 (m, 4H, N(C**H**$_2$CH$_2$)$_2$), 1.88 (brs, 4H, N(CH$_2$C**H**$_2$)$_2$), 1.15 (d, *J* = 7.2 Hz, 3H, CCHC**H**$_3$), 0.95 (d, *J* = 6.6 Hz, 3H, CH_2=CHCHCH_3); LRMS (CI) *m/z* 313 $(M)^+$; HRMS (CI) exact mass calc d for ($C_{20}H_{27}NO_2$) requires *m/z* 313.2042, found *m/z* 313.2035.

The yield was determined by enamine hydrolysis according to procedure B using 3 mL solvent and 1.5 g silica gel to provide the beta keto ester as a colorless oil in 94% yield (140 mg, 0.54 mmol). IR (thin film) 3068, 3035, 2973, 1746, 1713, 1642, 1456, 1419, 1376, 1313, 1223, 1160 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.38 (m, 5H, Ar**H**), 5.55-5.67 (m, 1H, CH_2=C**H**), 5.18 (s, 2H, C**H**$_2$Ph), 5.05 (d, *J* = 4.9 Hz, 1H, C**H**$_2$=CH), 5.00 (s, 1H, C**H**$_2$=CH), 3.53 (s, 2H, C(O)C**H**$_2$), 2.44-2.55 (m, 2H, CC**H**CH_3 and CH_2=CHC**H**CH_3), 1.04 (d, *J* = 6.6 Hz, 3H, CCHC**H**$_3$), 0.99 (d, *J* = 6.6 Hz, 3H, CH_2=CHCHC**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.8, 167.1, 140.4, 135.6, 128.8,

128.6, 128.6, 115.7, 67.3, 51.9, 48.9, 40.5, 18.7, 14.2; LRMS (CI) *m/z* 260.2 $(M)^+$; HRMS (CI) exact mass calc d for ($C_{16}H_{20}O_3$) requires *m/z* 260.1412, found *m/z* 260.1404.

The diastereomer ratio was determined by derivitization of the product to benzyl (2E,4*R**,5*S**)-4,5-dimethylhepta-2,6-dienoate according to general procedure C and analysis by ^{1}H NMR. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.39 (m, 5H, ArH), 6.94 (dd, *J* = 8.0, 15.7 Hz, 1H, C**H**=CHCO$_2$), 5.83 (d, *J* = 15.3 Hz, 1H, CH=C**H**CO$_2$), 5.61-5.73 (m, 1H, CH$_2$=C**H**), 5.18 (s, 2H, C**H**$_2$Ph), 5.02 (s, 1H, C**H**$_2$=CH), 4.97-4.99 (m, 1H, C**H**$_2$=CH), 2.12-2.28 (m, 2H, 2CH$_3$C**H**), 1.01 (d, *J* = 6.6 Hz, 3H, C**H**$_3$), 0.97 (d, *J* = 7.2 Hz, 3H, C**H**$_3$); LRMS (CI) *m/z* 245.2 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{16}H_{21}O_2$) requires *m/z* 245.1541, found *m/z* 245.1544.

Benzyl (2*E/Z*,4*R,5*S**)-4,5-Dimethyl-5-phenyl-3-pyrrolidinohepta-2,6-dienoate:** Prepared according to general procedure A from (*E*)-3-methyl cinnamyl pyrrolidine (69 mg, 0.34 mmol), benzyl penta-2,3-dienoate (54 mg, 0.29 mmol), and Zn(OTf)$_2$ (10 mg, 0.03 mmol). The crude residue was purified by silica gel chromatography (10% EtOAc:hexanes) to afford the title compound as a light yellow oil in 90% yield (100 mg, 0.26 mmol), 97:3 *syn:anti*, 40:60 *E:Z*. *Syn* isomer: IR (thin film) 3087, 3060, 3031, 2974, 2877, 1747, 1678, 1558, 1496, 1454, 1398, 1378, 1344, 1327, 1263, 1162, 1131, 1089, 1026, 919 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19-7.49 (m, 10H, Ar**H**), 6.41 (dd, *J* = 10.4, 16.5 Hz, 1H, CH$_2$=C**H,** *E* isomer), 6.32 (dd, *J* = 10.2, 16.8 Hz, 1H, CH$_2$=C**H** *Z* isomer), 5.50 (q, *J* = 7.7 Hz, 1H, C**H**CH$_3$ *E* isomer), 5.03-4.82 (m, 4H, C**H**$_2$Ph and C**H**$_2$=CH), 4.67 (s, 1H, NC=C**H** *E* isomer), 4.61 (s, 1H, NC=C**H** *Z* isomer), 3.44-3.52 (m, 2H, NC**H**$_2$ *Z* isomer), 3.12-3.24 (m, 3H, NC**H**$_2$ and C**H**CH$_3$ *Z* isomer), 2.96-3.03 (m, 2H,

NC**H**$_2$ *E* isomer), 2.78-2.85 (m, 2H, NC**H**$_2$ *E* isomer), 1.59-1.81 (m, 4H, N(CH_2C**H**$_2$)$_2$) (*E* and *Z* isomer), 1.56 (s, 3H, CC**H**$_3$) (*E* isomer), 1.53 (s, 3H, CC**H**$_3$) (*Z* isomer), 1.14 (d, *J* = 7.7 Hz, 3H, CHC**H**$_3$) (*E* isomer), 0.97 (d, *J* = 7.1 Hz, 3H, CHC**H**$_3$ *Z* isomer); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 166.0, 164.1, 163.5, 147.1, 145.9, 145.6, 144.5, 138.2, 138.0, 129.0, 128.8, 128.6, 128.6, 128.4, 128.3, 128.1, 128.1, 128.0, 127.8, 127.7, 127.7, 126.5, 126.2, 114.0. 112.8, 88.8, 84.9, 64.8, 64.7, 52.1, 50.5, 48.5, 48.4, 46.3, 40.5, 26.4, 25.8, 25.5, 25.1, 23.4, 22.0, 16.7, 14.5; LRMS (CI) *m/z* 388 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{26}H_{30}NO_2$) requires *m/z* 388.2277, found *m/z* 388.2264.

The diastereomer ratio was determined by derivitization of the product to benzyl (2*E*,4*R**,5*R**)-4,5-dimethyl-5-phenylhepta-2,6-dienoate according to general procedure C and analysis by GLC with a CC-1701 column (100 °C, 20 °C/min gradient), t_r 16.1 and 16.2 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18-7.41 (m, 10H, Ar**H**), 7.01 (dd, *J* = 7.1, 15.9 Hz, 1H, C**H**=$CHCO_2$), 5.84 (d, *J* = 15.9 Hz, 1H, CH=C**H**CO_2), 5.19 (dd, *J* = 1.1, 11.0 Hz, 1H, C**H**$_2$=CH), 5.16 (s, 2H, C**H**$_2$Ph), 5.05 (d, *J* = 17.0 Hz, 1H, C**H**$_2$=CH), 2.90 (dq, *J* = 6.6, 7.1 Hz, 1H, C**H**CH_3), 1.38 (s, 3H, CC**H**$_3$), 0.91 (d, *J* = 6.6 Hz, 3H, CHC**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 152.2, 146.2, 144.4, 136.3, 128.7, 128.4, 128.3, 128.3, 126.9, 121.5, 114.3, 66.3, 47.7, 45.1, 21.4, 14.6; LRMS (CI) *m/z* 321.2 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{22}H_{25}O_2$) requires *m/z* 321.1854, found *m/z* 321.1852.

Benzyl (2*E*,4*R,5*S**)-5-Isopropyl-4-methyl-3-pyrrolidinohepta-2,6-dienoate:** Prepared according to general procedure A from (*E*)-4-methyl-2-pentenyl pyrrolidine (176 mg, 1.15 mmol), benzyl penta-2,3-dienoate (108 mg, 0.57 mmol), and $Zn(OTf)_2$ (20 mg, 0.06 mmol) to provide the crude enamine as a yellow oil in 81% yield (159 mg, 0.47

mmol), >98:2 *syn:anti*, 5:1 *E:Z*. *Syn, E* isomer: IR (thin film) 3067, 3032, 2961, 2873, 1742, 1678, 1560, 1455, 1424, 1400, 1345, 1310, 1258, 1129, 1060, 1026 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24-7.40 (m, 5H, Ar**H**), 5.60 (ddd, *J* = 10.2, 10.2, 17.3 Hz, 1H, CH_2=C**H**), 5.03-5.18 (m, 3H, CNC**H**CH_3 and C**H**$_2$Ph), 4.92 (dd, *J* = 2.2, 10.2 Hz, 1H, C**H**$_2$=CH), 4.79 (dd, *J* = 2.2, 17.0 Hz, 1H, C**H**$_2$=CH), 4.44 (s, 1H, NC=C**H**), 3.24-3.35 (m, 4H, N(C**H**$_2$)$_2$), 2.09 (ddd, *J* = 2.5, 10.7, 10.7 Hz, 1H, $(CH_3)_2$CHC**H**), 1.80-1.98 (m, 5H, $(CH_3)_2$C**H** and N(CH_2C**H**$_2$)$_2$), 1.22 (d, *J* = 7.1 Hz, 3H, CNCHC**H**$_3$), 0.94 (d, *J* = 7.1 Hz, 3H, (C**H**$_3$)$_2$CH), 0.89 (d, *J* = 6.6 Hz, 3H, (C**H**$_3$)$_2$CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 166.6, 137.9, 128.5, 128.1, 115.5, 84.7, 64.5, 53.8, 49.7, 33.2, 28.6, 25.5, 22.5, 16.5, 16.4; LRMS (CI) *m/z* 342.2 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{22}H_{33}NO_2$) requires *m/z* 342.2432, found *m/z* 342.2434.

The diastereomer ratio was determined by derivitization of the product to benzyl (2*E*,4*R**,5*R**)-5-isopropyl-4-methylhepta-2,6-dienoate according to general procedure C and analysis by ^1H NMR. ^1H NMR (300 MHz, $CDCl_3$) δ 7.29-7.40 (m, 5H, Ar**H**), 6.95 (dd, *J* = 8.4, 15.8 Hz, 1H, C**H**=CHCO_2), 5.83 (dd, *J* = 1.1, 15.6 Hz, 1H, CH=C**H**CO_2), 5.46 (ddd, *J* = 10.1, 10.1, 17.0 Hz, 1H, CH_2=C**H**), 5.18 (s, 2H, C**H**$_2$Ph), 5.09 (dd, *J* = 2.2, 10.1 Hz, 1H, C**H**$_2$=CH), 4.94 (dd, 2.2, 16.7 Hz, 1H, C**H**$_2$=CH), 2.53-2.64 (m, 1H, C**H**CH=CH), 1.62-1.74 (m, 2H, iPr-C**H** and C**H**$(CH_3)_2$), 1.02 (d, *J* = 7.0 Hz, 3H, C**H**$_3$), 0.92 (d, *J* = 6.1 Hz, 3H, C**H**$_3$), 0.82 (d, *J* = 6.6 Hz, 3H, C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 153.1, 137.5, 136.3, 128.7, 128.4, 128.3, 120.6, 117.8, 66.3, 57.1, 37.6, 28.9, 21.5, 20.2, 18.7; LRMS (CI) *m/z* 273.2 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{18}H_{25}O_2$) requires *m/z* 273.1854, found *m/z* 273.1850.

Benzyl (2*E*,4*R,5*S**)-3-Dimethylamino-4-methyl-5-phenylhepta-2,6-dienoate**: Prepared according to general procedure A from (*E*)-cinnamyl-*N,N*-dimethylamine (185 mg, 1.15 mmol), benzyl penta-2,3-dienoate (108 mg, 0.57 mmol), and $Zn(OTf)_2$ (20 mg, 0.06 mmol). The crude residue was purified by silica gel chromatography (5% EtOAc:hexanes) to provide the title compound as white needles in 81% yield (162 mg, 0.46 mmol), 94:6 *syn:anti*, 6:1 *E:Z*. *Syn*, *E* isomer IR (thin film) 3063, 3029, 2971, 2936, 1678, 1569, 1494, 1454, 1397, 1372, 1316, 1130, 1041, 1024 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.22-7.43 (m, 10H, Ar**H**), 6.03 (ddd, *J* = 9.4, 9.4, 17.7 Hz, 1H, CH_2=C**H**), 5.46 (dq, *J* = 7.0, 11.6 Hz, 1H, C**H**CH_3), 5.18 (d, *J* = 9.2 Hz, 1H, C**H**$_2$Ph), 5.13 (d, *J* = 9.2 Hz, 1H, C**H**$_2$Ph), 4.86-4.93 (m, 2H, C**H**$_2$=CH), 4.66 (s, 1H, NC=C**H**), 3.47 (dd, *J* = 10.3, 10.5 Hz, 1H, C**H**Ph), 3.00 (s, 6H, N(C**H**$_3$)$_2$), 1.02 (d, *J* = 7.5 Hz, 3H, CHC**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0, 167.9, 143.7, 141.5, 137.8, 129.0, 128.7, 128.3, 128.2, 127.9, 126.8, 114.1, 87.0, 64.9, 55.9, 41.9, 36.5, 16.8; LRMS (CI) *m/z* 350.2 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{22}H_{28}NO_2$) requires *m/z* 350.2120, found *m/z* 350.2114.

The diastereomer ratio was determined by derivitization of the product to benzyl (2*E*,4*R**,5*S**)-4-methyl-5-phenylhepta-2,6-dienoate according to general procedure C and analysis by ^1H NMR.

Benzyl (2*E*,4*R,5*S**)-3-Piperidino-4-methyl-5-phenylhepta-2,6-dienoate**: Prepared according to general procedure A from (*E*)-cinnamyl piperidine (232 mg, 1.15 mmol), benzyl penta-2,3-dienoate (108 mg, 0.57 mmol), and $Zn(OTf)_2$ (20 mg, 0.06 mmol). The crude residue was purified by silica gel chromatography (5% EtOAc:hexanes) to provide

the title compound as a yellow oil in 87% yield (194 mg, 0.50 mmol), 94:6 *syn:anti*, 6:1 *E:Z*. *Syn*, *E* isomer: IR (thin film) 3062, 3029, 2936, 2856, 1746, 1683, 1565, 1494, 1454, 1396, 1360, 1253, 1233, 1145, 1124, 1080, 1022 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.18-7.45 (m, 10H, Ar**H**), 5.99-6.11 (m, 1H, CH_2=C**H**), 5.36 (brs, 1H, C**H**CH_3), 5.17 (s, 2H, C**H**$_2$Ph), 4.88-4.94 (m, 3H, C**H**$_2$=CH and NC=C**H**), 3.41-3.47 (m, 1H, PhC**H**), 3.29-3.31 (m, 4H, N(CH_3)$_2$), 1.64 (brs, 6H, piperdine), 1.01 (d, *J* = 7.5 Hz, 3H, C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 166.5, 143.8, 141.6, 137.7, 128.9, 128.7, 128.4, 128.3, 127.9, 126.7, 114.5, 89.0, 65.0, 56.1, 49.9, 36.8, 27.5, 26.1, 24.7; LRMS (CI) *m/z* 390.2 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{26}H_{31}NO_2$) requires *m/z* 389.2354, found *m/z* 390.2432.

The diastereomer ratio was determined by derivitization of the product to benzyl (2*E*,4*R**,5*R**)-4-methyl-5-phenylhepta-2,6-dienoate according to general procedure C and analysis by ^1H NMR.

Benzyl (2*E*,4*R,5*S**)-4,5,9-Trimethyl-3-pyrrolidinohepta-5-vinyldeca-2,8-dienoate:** Prepared according to general procedure A from geranyl pyrrolidine (178 mg, 0.86 mmol), benzyl penta-2,3-dienoate (108 mg, 0.57 mmol), and $Zn(OTf)_2$ (10 mg, 0.03 mmol). The crude residue was purified by silica gel chromatography (10% EtOAc:hexanes) to provide the title compound as a yellow oil in 94% yield (214 mg, 0.54 mmol), >98:2 *syn:anti*, 2:3 *E:Z*. *Syn* isomer: IR (thin film) 2971, 2876, 1681, 1561, 1454, 1414, 1397, 1378, 1345, 1320, 1263, 1161, 1129, 1093, 1026 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25-7.40 (m, 5H, Ar**H**), 5.84 (dd, *J* = 11.0, 17.6, Hz, 1H, CH_2=C**H** *Z* isomer), 5.74 (dd, *J* = 11.0, 17.6 Hz, 1H, CH_2=C**H** *E* isomer), 4.91-5.17 (m, 6H,

C**H**$_2$=CH, C**H**$_2$Ph, $(CH_3)_2$C=C**H** *E* and *Z* isomer; and C**H**CH_3 *Z* isomer), 4.63 (s, 1H, NC=C**H** *E* isomer), 4.57 (s, 1H, NC=C**H** *Z* isomer), 3.59-3.67 (m, 2H, N(C**H**$_3)_2$ *Z* isomer), 3.43-3.48 (m, 2H, N(C**H**$_3)_2$ *E* isomer), 3.24-3.29 (m, 2H, N(C**H**$_3)_2$ *Z* isomer), 3.10-3.18 (m, 2H, N(C**H**$_3)_2$ *E* isomer), 2.69 (q, *J* = 7.1 Hz, 1H, C**H**CH_3 *E* isomer), 1.74-1.95 (m, 6H, N(CH_2C**H**$_2)_2$ and CHC**H**$_2$ *E* and *Z* isomer), 1.67 (s, 3H, C**H**$_3$), 1.57 and 1.56 (s, 3H, C**H**$_3$), 1.37-1.49 (m, 2H, $CHCH_2$C**H**$_2$ *E* and *Z* isomer), 1.17 (d, *J* = 7.7 Hz, 3H, CHC**H**$_3$ *E* isomer), 1.12 (s, 3H, C**H**$_3$ *E* isomer), 1.05-1.07 (m, 6H, C**H**$_3$ *E* and *Z* isomer); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 166.1, 164.9, 164.8, 144.9, 143.6, 138.2, 138.0, 131.5, 130.8, 128.6, 128.5, 128.0, 128.0, 127.7, 127.7, 125.6, 124.9, 113.8, 113.8, 88.4, 85.6, 64.7, 64.5, 52.3, 50.6, 45.0, 44.1, 44.0, 39.8, 39.2, 39.1, 26.1, 26.1, 26.0, 25.0, 23.7, 23.5, 20.9, 20.4, 18.1, 18.1, 16.3, 14.2; LRMS (CI) *m/z* 396.3 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{26}H_{37}NO_2$) requires *m/z* 396.2902, found *m/z* 396.2899.

The diastereomer ratio was determined by derivitization of the product to benzyl (2*E*,4*R**,5*R**)-4,5,9-Trimethyl-5-vinyldeca-2,6-dienoate according to general procedure C and analysis by ^{1}H NMR. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.37 (m, 5H, Ar**H**), 7.01 (dd, *J* = 8.5, 15.6 Hz, 1H C**H**=$CHCO_2$), 5.83 (d, *J* = 15.4 Hz, 1H, CH=C**H**CO_2), 5.71 (dd, *J* = 11.0, 17.6 Hz, 1H, CH_2=C**H**), 5.18 (s, 2H, C**H**$_2$Ph), 5.04-5.13 (m, 2H, C**H**$_2$=CH and $(CH_3)_2$=C**H**), 4.95 (d, *J* = 17.0 Hz, 1H, C**H**$_2$=CH), 2.26 (dq, *J* = 7.1, 7.4 Hz, 1H, C**H**CH_3), 1.84-1.87 (m, 2H, C=CHC**H**$_2$), 1.67 (s, 3H, C**H**$_3$), 1.57 (s, 3H, C**H**$_3$), 1.33 (t, *J* = 8.5 Hz, 2H, C=$CHCH_2$C**H**$_2$), 1.00 and 0.97 (d and s, 6H, CHC**H**$_3$ and CC**H**$_3$); LRMS (CI) *m/z* 327.2 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{22}H_{31}O_2$) requires *m/z* 327.2324, found *m/z* 327.2326.

Benzyl (2*E*,4*R,5*R**)-4,5,9-Trimethyl-3-pyrrolidinohepta-5-vinyldeca-2,8-dienoate:** Prepared according to general procedure A from neryl pyrrolidine (178 mg, 0.86 mmol), benzyl penta-2,3-dienoate (108 mg, 0.57 mmol), and $Zn(OTf)_2$ (10 mg, 0.03 mmol). The crude residue was purified by silica gel chromatography (10% EtOAc:hexanes) to provide the title compound as a yellow oil in 93% yield (211 mg, 0.53 mmol), >98:2 *syn:anti*, 1:1. IR (thin film) 2970, 2876, 1680, 1560, 1455, 1413, 1398, 1376, 1344, 1319, 1264, 1161, 1130, 1091, 1026 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24-7.39 (m, 5H, Ar**H**), 5.95 (dd, *J* = 11.0, 17.6 Hz, 1H, CH_2=C**H**), 5.72 (dd, *J* = 11.0, 17.6 Hz, 1H, CH_2=C**H**), 4.91-5.19 (m, 6H, C**H**$_2$=CH, C**H**$_2$Ph, $(CH_3)_2$C=C**H** and C**H**CH_3), 4.61 (s, 1H, NC=C**H**), 4.59 (s, 1H, NC=C**H**), 3.09-3.62 (m, 4H, N(C**H**$_3)_2$), 2.68 (q, *J* = 7.1 Hz, 1H, C**H**CH_3), 1.74-1.97 (m, 6H, N(CH_2C**H**$_2)_2$ and CHC**H**$_2$), 1.67 (s, 3H, C**H**$_3$), 1.57 and 1.56 (s, 3H, C**H**$_3$), 1.26-1.50 (m, 2H, $CHCH_2$C**H**$_2$), 1.03-1.21 (m, 6H, 2C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 166.1, 165.2, 164.7, 145.4, 144.5, 138.3, 138.0, 131.4, 131.0, 128.5, 128.5, 128.1, 128.0, 127.7, 127.6, 125.3, 124.9, 114.3, 113.1, 87.5, 84.2, 64.6, 64.5, 52.3, 50.5, 45.2, 43.9, 42.8, 40.2, 40.1, 38.5, 26.1, 26.1, 26.0, 25.1, 23.3, 23.3, 19.9, 19.5, 18.1, 18.1, 16.3, 13.4; LRMS (CI) *m/z* 396.3 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{26}H_{37}NO_2$) requires *m/z* 396.2902, found *m/z* 396.2901.

The diastereomer ratio was determined by derivitization of the product to benzyl (2*E*,4*R**,5*S**)-4,5,9-Trimethyl-5-vinyldeca-2,6-dienoate according to general procedure C and analysis by ^1H NMR. ^1H NMR (300 MHz, $CDCl_3$) δ 7.33-7.37 (m, 5H, Ar**H**), 6.98 (dd, *J* = 9.3, 15.9 Hz, 1H C**H**=$CHCO_2$), 5.85 (d, *J* = 15.9 Hz, 1H, CH=C**H**CO_2), 5.67 (dd, *J* = 11.0, 17.3 Hz, 1H, CH_2=C**H**), 5.18 (s, 2H, C**H**$_2$Ph), 5.12 (d, *J* = 11.0 Hz, 1H, C**H**$_2$=CH), 5.06 (t, *J* = 6.9 Hz, 1H, $(CH_3)_2$=C**H**), 4.95 (d, *J* = 17.6 Hz, 1H, C**H**$_2$=CH),

2.24 (dq, *J* = 7.1, 7.7 Hz, 1H, C**H**CH_3), 1.85 (dt, *J* = 7.4, 8.2 Hz, 2H, C=CHC**H**$_2$), 1.67 (s, 3H, C**H**$_3$), 1.57 (s, 3H, C**H**$_3$), 1.25-1.37 (m, 2H, C=$CHCH_2$C**H**$_2$), 0.97 and 0.95 (d and s, 6H, CHC**H**$_3$ and CC**H**$_3$); LRMS (CI) *m/z* 327.2 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{22}H_{31}O_2$) requires *m/z* 327.2324, found *m/z* 327.2318.

Methyl (2*E*,4*R,5*R**)-4-Phenyl-5-methyl-3-pyrrolidinohepta-2,6-dienoate**: Prepared according to general procedure A from crotyl pyrrolidine (118 mg, 0.94 mmol), methyl 4-phenylbuta-2,3-dienoate (82 mg, 0.47 mmol), and $Zn(OTf)_2$ (17 mg, 0.05 mmol). The crude residue was purified by silica gel chromatography (5% EtOAc:hexanes) to afford the title compound as a crystalline solid in 86% yield (121 mg, 0.40 mmol), 97:3 *syn:anti*, 10:1 *E/Z*. *Syn*, *E* isomer: IR (thin film) 2973, 2869, 1675, 1561, 1496, 1449, 1422, 1385, 1345, 1281, 1141 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14-7.36 (m, 5H, ArH), 6.15 (brd, *J* = 9.9 Hz, 1H, CHPh), 5.85 (ddd 9.6, 9.6, 17.1 Hz, CH_2=CH), 4.96 (dd, *J* = 1.8, 17.1 Hz, 1H, CH_2=CH), 4.87 (dd, *J* = 2.0, 10.1 Hz, 1H, CH_2=CH), 4.57 (s, 1H, NC=CH), 3.67 (s, 3H, OCH_3), 2.90-3.21 (m, 5H, $CHCH_3$ and $N(CH_2CH_2)_2$), 1.61-1.71 (m, 4H, $N(CH_2CH_2)_2$), 1.28 (d, *J* = 6.3 Hz, 3H, $CHCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.9, 164.0, 142.7, 139.4, 128.4, 128.4, 126.0, 112.8, 85.7, 50.4, 49.1, 47.0, 37.9, 25.3, 21.5; LRMS (CI) *m/z* 299 $(M)^+$; HRMS (CI) exact mass calc d for ($C_{19}H_{25}NO_2$) requires *m/z* 299.1885, found *m/z* 299.1878.

The diastereomer ratio was determined by derivitization of the product to methyl (2*E*,4*R**,5*R**)-5-methyl-4-phenylhepta-2,6-dienoate according to general procedure C and analysis by ^{1}H NMR. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10-7.35 (m, 6H, Ar**H** and C**H**=$CHCO_2$), 5.67-5.79 (m, 2H, CH=C**H**CO_2 and CH_2=C**H**), 5.07 (d, *J* = 5.5 Hz, 1H,

C**H**$_2$=CH), 5.03 (s, 1H, C**H**$_2$=CH), 3.69 (s, 3H, $CO_2C\mathbf{H}_3$), 3.20 (t, *J* = 8.8 Hz, 1H, PhC**H**), 2.54-2.67 (m, 1H, CHC**H**$_3$), 0.89 (d, *J* = 6.6 Hz, 3H, CHC**H**$_3$); LRMS (CI) *m/z* 231.1 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{15}H_{19}O_2$) requires *m/z* 231.1385, found *m/z* 231.1382.

Methyl (2*E*,4*R,5*R**)-4,5-Diphenyl-3-pyrrolidinohepta-2,6-dienoate:** Prepared according to general procedure A from cinnamyl pyrrolidine (108 mg, 1.15 mmol), methyl 4-phenylbuta-2,3-dienoate (100 mg, 0.57 mmol), and $Zn(OTf)_2$ (20 mg, 0.06 mmol). The crude residue was purified by silica gel chromatography (5% EtOAc:hexanes) to afford the title compound as a colorless oil in 94% yield (196 mg, 0.54 mmol), 94:6 *syn:anti*. *Syn* isomer: IR (thin film) 2974, 2944, 1671, 1562, 1495, 1448, 1422, 1384, 1345, 1280, 1180, 1141 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02-7.59 (m, 11H, Ar**H** and NCC**H**Ph), 5.98 (ddd, *J* = 9.8, 9.8, 16.6 Hz, 1H, CH_2=C**H**), 4.95 (d, *J* = 17.1 Hz, 1H, C**H**$_2$=CH), 4.84 (dd, *J* = 1.2, 9.9 Hz, 1H, C**H**$_2$=CH), 4.72 (s, 1H, NC=C**H**), 4.14 (dd, *J* = 10.1, 10.0 Hz, 1H, CH_2=CHC**H**), 3.73 (s, 3H, OC**H**$_3$), 2.99-3.29 (m, 4H, $N(CH_2C\mathbf{H}_2)_2$), 1.66-1.75 (m, 4H, $N(CH_2C\mathbf{H}_2)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 163.1, 143.2, 141.7, 139.3, 129.1, 128.6, 128.2, 128.1, 126.6, 125.9, 113.1, 86.8, 51.2, 50.6, 49.3, 44.4, 25.4; LRMS (CI) *m/z* 361 $(M)^+$; HRMS (CI) exact mass calc d for ($C_{24}H_{27}NO_2$) requires *m/z* 361.2042, found *m/z* 361.2041.

The diastereomer ratio was determined by derivitization of the product to methyl (2*E*,4*R**,5*R**)-4,5-diphenylhepta-2,6-dienoate according to general procedure C and analysis by ^{1}H NMR. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02-7.28 (m, 11H, Ar**H** and C**H**=$CHCO_2$), 6.07 (ddd, *J* = 8.2, 10.4, 17.0 Hz, 1H, CH_2=C**H**), 5.82 (d, *J* = 15.9 Hz, 1H,

CH=C**H**CO_2), 5.08-5.16 (m, 2H, C**H**$_2$=CH), 3.68-3.82 (m, 2H, 2C**H**Ph), 3.72 (s, 3H, C**H**$_3$); LRMS (CI) *m/z* 293.2 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{20}H_{21}O_2$) requires *m/z* 293.1541, found *m/z* 293.1543.

(*E*)-Benzyl 5-Phenyl-3-Pyrrolidinohepta-2,6-dienoate: Prepared according to general procedure A from cinnamyl pyrrolidine (108 mg, 0.57 mmol), benzyl buta-2,3-dienoate (100 mg, 0.57 mmol), and $Zn(OTf)_2$ (10 mg, 0.03 mmol) to afford the title compound as a clear oil in 84% yield (174 mg, 0.48 mmol). The material was homogeneous by ^{1}H NMR and ^{13}C NMR analysis. IR (thin film) 3062, 3029, 2973, 2950, 2871, 1678, 1562, 1495, 1483, 1449, 1387, 1345, 1182, 1128, 1056, 1037, 916 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18-7.42 (m, 10H, Ar**H**), 6.17 (ddd, *J* = 6.6, 10.4, 17.0, 1H, CH_2=C**H**), 5.09-5.18 (m, 4H, C**H**$_2$Ph, C**H**$_2$=CH), 4.58 (s, 1H, NC=C**H**), 3.76-3.80 (m, 2H, CHC**H**$_2$), 2.84-3.12 (brm, 5H, C**H**CH_2 and N(C**H**$_2$$CH_2$)$_2$), 1.73 (brs, 4H, N($CH_2$C**H**$_2$)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 162.0, 143.6, 140.5, 138.1, 128.6, 128.5, 128.2, 128.2, 127.8, 126.7, 115,0, 84.0, 64.6, 49.2, 48.5, 36.5, 25.4; LRMS (CI) *m/z* 361 $(M)^+$; HRMS (CI) exact mass calc d for ($C_{24}H_{27}NO_2$) requires *m/z* 361.2042, found *m/z* 361.2042.

Benzyl (2*E*,4*R,5*S**)-4-Isopropyl-5-phenyl-3-pyrrolidinohepta-2,6-dienoate:** Prepared according to general procedure A from cinnamyl pyrrolidine (216 mg, 1.15 mmol), benzyl 5-methylhexa-2,3-dienoate (125 mg, 0.58 mmol), and $Zn(OTf)_2$ (20 mg, 0.06 mmol). The crude residue was purified by silica gel chromatography to afford the title compound as a yellow oil in 94% yield (219 mg, 0.54 mmol), 94:6 *syn/anti*, 7:1 *E/Z*. *Syn*, *E* isomer: IR (thin film) 3028, 2961, 2870, 1675, 1559, 1454, 1396, 1344, 1316,

1128, 1059, 1028 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.14-7.52 (m, 10H, Ar**H**), 5.93 (ddd, *J* = 9.9, 9.9, 17.0 Hz, 1H, CH_2=C**H**), 5.31 (dd, *J* = 9.9, 9.9 Hz, 1H, C**H**CH(CH_3)$_2$), 5.21 (d, *J* = 12.6 Hz, 1H, C**H**$_2$Ph), 5.16 (d, *J* = 12.6 Hz, 1H, C**H**$_2$Ph), 4.85 (d, *J* = 17.0 Hz, 1H, C**H**$_2$=CH), 4.75 (dd, *J* = 1.4, 10.2 Hz, 1H C**H**$_2$=CH), 4.67 (s, 1H, NC=C**H**), 3.26-3.57 (m, 5H, PhC**H** and N(C**H**$_2$)$_2$), 1.80-2.01 (m, 5H, C**H**(CH_3)$_2$ and N(CH_2CH_2)$_2$), 0.85 (d, *J* = 6.59 Hz, 3H, C**H**$_3$), 0.53 (d, *J* = 6.59 Hz, 3H, C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2, 164.1, 146.0, 142.6, 138.0, 128.7, 128.6, 128.6, 128.2, 128.1, 127.8, 126.4, 112.1, 87.2, 64.7, 55.3, 50.1, 48.7, 31.7, 25.5, 23.9, 22.6; LRMS (CI) 404.3 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{27}H_{34}NO_2$) requires *m/z* 404.2589, found *m/z* 404.2594.

The diastereomer ratio was determined by derivitization of the product to benzyl (2*E*,4*R**,5*R**)-4-isopropyl-5-phenylhepta-2,6-dienoate according to general procedure C and analysis by ^1H NMR. ^1H NMR (300 MHz, $CDCl_3$) δ 7.16-7.40 (m, 10H, Ar**H**), 6.88 (dd, *J* = 10.4, 15.4 Hz, 1H, C**H**=$CHCO_2$), 5.80-5.92 (m, 1H, CH_2=C**H**), 5.81 (d, *J* = 15.4 Hz, 1H, CH=C**H**CO_2), 5.20 (s, 2H, C**H**$_2$Ph), 5.00 (d, *J* = 4.4 Hz, 1H, C**H**$_2$=CH), 4.95 (d, *J* = 11.0 Hz, 1H, C**H**$_2$=CH), 3.44 (dd, *J* = 9.1, 9.1 Hz, 1H, C**H**Ph), 2.41 (ddd, *J* = 10.2, 4.1, 10.1 Hz, 1H, iPrC**H**), 1.54-1.64 (m, 1H, (CH_3)$_2$C**H**), 0.83 (d, *J* = 4.4 Hz, 3H, (C**H**$_3$)$_2$CH), 0.81 (d, *J* = 4.4 Hz, 3H, (C**H**$_3$)$_2$CH); LRMS (CI) 335.2 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{23}H_{25}O_2$) requires *m/z* 335.2010, found *m/z* 335.2016.

Benzyl (2*E*,4*S,5*S**)-4-Chloro-5-phenyl-3-pyrrolidinohepta-2,6-dienoate:** Prepared according to general procedure A from cinnamyl pyrrolidine (180 mg, 1.00 mmol), benzyl 4-chlorobuta-2,3-dienoate (100 mg, 0.48 mmol), and $Zn(OTf)_2$ (17 mg,

0.05 mmol). The crude residue was purified by silica gel chromatography to afford the title compound as a yellow oil in 84% yield (160 mg, 0.40 mmol), 93:7 *syn:anti*, 7:1 *E:Z*. *Syn*, *E* isomer: IR (thin film) 3503, 1670, 1570, 1456, 1395, 1345, 1133 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.30-7.52 (m, 11H, Ar**H** and C**H**Cl), 6.02 (ddd, *J* = 9.1, 9.1, 17.6 Hz, 1H, CH_2=C**H**), 5.25 (d, *J* = 12.6 Hz, 1H, C**H**$_2$Ph), 5.19 (d, *J* = 12.0 Hz, 1H, C**H**$_2$Ph), 5.03 (d, *J* = 16.5 Hz, 1H, C**H**$_2$=CH), 5.02 (d, *J* = 9.9 Hz, 1H C**H**$_2$=CH), 4.71 (s, 1H, NC=C**H**), 3.92 (dd, *J* = 10.2, 10.2 Hz, 1H, PhC**H**), 3.72 (brs, 2H, N(C**H**$_2$)$_2$), 3.41-3.44 (m, 2H, N(C**H**$_2$)$_2$, 1.90-1.97 (m, 4H, N(CH_2C**H**$_2$)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 157.4, 141.3, 138.1, 137.4, 129.1, 128.7, 128.3, 128.3, 128.1, 127.4, 116.6, 87.4, 65.3, 56.5, 56.1, 50.0, 25.6; LRMS (CI) 395.1 $(M)^+$; HRMS (CI) exact mass calc d for ($C_{24}H_{24}ClNO_2$) $(M-H)^+$ requires *m/z* 394.1574, found *m/z* 394.1569.

The diastereomer ratio was determined by derivatization of the product to benzyl (2*E*,4*R**,5*S**)-4-chloro-5-phenylhepta-2,6-dienoate according to general procedure C and analysis by ^1H NMR. ^1H NMR (300 MHz, $CDCl_3$) δ 7.23-7.40 (m, 10H, Ar**H**), 7.00 (dd, *J* = 8.2, 15.4 Hz, 1H, C**H**=$CHCO_2$), 5.89-6.22 (m, 1H, CH_2=C**H**), 6.08 (d, ***J*** = 15.4 Hz, 1H, CH=C**H**CO_2), 5.09-5.25 (m, 2H, C**H**$_2$=CH), 5.21 (s, 2H, C**H**$_2$Ph), 4.73 (t, *J* = 7.7 Hz, 1H, C**H**Cl), 3.72 (t, *J* = 8.0 Hz, 1H, C**H**Ph). LRMS (CI) 327.0 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{20}H_{20}ClO_2$) requires *m/z* 327.1152, found *m/z* 327.1148.

Benzyl (2*E*,4*S,5*S**)-5-Phenyl-4-phthalimido-3-pyrrolidinohepta-2,6-dienoate:** Prepared according to general procedure A from cinnamyl pyrrolidine (64 mg, 0.34 mmol), benzyl 4-phthalimidobuta-2,3-dienoate (91 mg, 0.28 mmol), and $Zn(OTf)_2$ (10 mg, 0.03 mmol). The crude residue was purified by silica gel chromatography (20%

EtOAc:hexanes) to afford the title compound as a yellow solid in 75% yield (108 mg, 0.21 mmol) 91:9 *syn/anti*, 1:1 *E:Z*. The (*E*)-product isomer was recrystallized from EtOAc/hexanes. *Syn* isomer: IR (thin film) 3062, 3030, 2975, 2871, 1773, 1715, 1676, 1571, 1456, 1379, 1346, 1320, 1133 cm^{-1}; *E* isomer: ^1H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 11.5 Hz, 1H, C**H**N), 7.10-7.69 (m, 14H, Ar**H**), 6.04 (ddd, *J* = 9.3, 9.3, 16.9 Hz, 1H, CH_2=C**H**), 5.29 (s, 2H, C**H**$_2$Ph), 4.90-5.14 (m, 3H, C**H**$_2$=CH and PhC**H**), 4.83 (s, 1H, NC=C**H**), 3.63-3.68 (m, 2H, N(C**H**$_2$)$_2$), 3.16-3.18 (m, 2H, N(C**H**$_2$)$_2$), 1.74-2.05 (m, 4H, N(CH_2C**H**$_2$)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 168.7, 168.3, 166.6, 158.5, 156.9, 141.6, 139.9, 139.5, 137.9, 137.7, 137.5, 134.5, 134.4, 134.1, 131.6, 131.4, 128.9, 128.8, 128.6, 128.5, 128.3, 128.2, 128.0, 127.8, 127.7, 127.2, 126.9, 123.4, 123.3, 118.4, 115.5, 89.2, 85.9, 65.2, 65.0, 56.3, 54.2, 52.4, 51.9, 50.1, 49.0, 26.2, 25.7. LRMS (CI) 506 $(M)^+$; HRMS (CI) exact mass calc d for ($C_{32}H_{30}N_2O_4$) requires *m/z* 506.2206, found *m/z* 506.2206.

The diastereomer ratio was determined by derivitization of the product to benzyl (2*E*,4*R**,5*S**)-5-phenyl-4-phthalimidohepta-2,6-dienoate according to general procedure C and analysis by ^1H NMR. ^1H NMR (300 MHz, $CDCl_3$) δ 7.59-7.69 (m, 4H, phthalimide **H**), 7.28-7.42 (m, 6H, Ar**H** and C**H**=$CHCO_2$), 7.02-7.16 (m, 5H, Ar**H**), 5.91-6.03 (m, 2H, CH_2=C**H** and CH=C**H**CO_2), 5.15-5.26 (m, 5H, C**H**$_2$=CH and C**H**$_2$Ph and C**H**N), 4.38 (dd, *J* = 8.8, 11.5 Hz, 1H, C**H**Ph). LRMS (EI) 460.1 $(MNa)^+$; HRMS (EI) exact mass calc d for ($C_{28}H_{23}NO_4Na$) requires *m/z* 460.1525, found *m/z* 460.1541.

Benzyl (2*E*,4*R,5*S**)-4-Allyl-5-phenyl-3-pyrrolidinohepta-2,6-dienoate:** Prepared according to general procedure A from cinnamyl pyrrolidine (216 mg, 1.15 mmol),

benzyl 2,3,6-heptatrienoate (122 mg, 0.58 mmol), and $Zn(OTf)_2$ (20 mg, 0.06 mmol). The crude residue was purified by silica gel chromatography (5% EtOAc:hexanes) to afford the title compound as a yellow oil in 96% yield (219 mg, 0.55 mmol), 95:5 *syn:anti*, 2:1 *E:Z*. *Syn* isomer: IR (thin film) 3064, 3029, 2974, 2869, 1676, 1561, 1493, 1483, 1454, 1400, 1345, 1128, 1081, 1067, 1039, 1027 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.17-7.49 (m, 10H, Ar**H**), 6.09 (ddd, *J* = 9.3, 10.0, 16.9 Hz, 1H, CH_2=C**H**CHPh, *E* isomer), 5.96 (ddd, *J* = 8.2, 10.4, 17.0 Hz, 1H, CH_2=C**H**CHPh**,** *Z* isomer), 5.56-5.69 (m, 2H, C**H**allyl and CH_2=C**H**CH_2), 5.19 (s, 2H, C**H**$_2$Ph, *E* isomer), 5.17 (s, 2H, C**H**$_2$Ph, *Z* isomer), 4.82-4.95 (m, 4H, C**H**$_2$=CHCHPh and C**H**$_2$=$CHCH_2$), 4.72 (s, 1H, NC=C**H**, *Z* isomer), 4.70 (s, 1H, NC=C**H**, *Z* isomer), 3.37-3.52 (m, 4H, N(C**H**$_2$)$_2$), 3.07-3.13 (m, 1H, C**H**Ph), 2.09-2.28 (m, 2H, CH_2=CHC**H**$_2$), 1.86-1.93 (m, 4H, N(CH_2C**H**$_2$)$_2$; ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2, 167.3, 165.0, 162.9, 143.5, 143.2, 141.2, 140.8, 138.2, 138.0, 136.7, 136.7, 129.1, 129.0, 128.8, 128.7, 128.6, 128.3, 128.1, 128.0, 127.8, 127.7, 126.8, 126.6, 116.0, 115.9, 115.4, 114.1, 87.8, 84.4, 64.7, 64.7, 54.7, 50.8, 49.9, 49.8, 48.4, 42.5, 35.2, 34.4, 25.7, 25.6; LRMS (CI) 402.2 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{27}H_{32}NO_2$) requires *m/z* 402.2433, found *m/z* 402.2428.

The diastereomer ratio was determined by derivitization of the product to benzyl (2*E*,4*S**,5*S**)-4-allyl-5-phenylhepta-2,6-dienoate according to general procedure C and analysis by ^1H NMR. ^1H NMR (300 MHz, $CDCl_3$) δ 7.19-7.41 (m, 10H, Ar**H**), 6.91 (dd, *J* = 9.3, 15.9 Hz, 1H, C**H**=$CHCO_2$), 5.96 (ddd, *J* = 8.8, 10.0, 17.1 Hz, 1H, CH_2=C**H**CHPh), 5.85 (d, *J* = 15.4 Hz, 1H, CH=C**H**CO_2), 5.61-5.75 (m, 1H, CH_2=C**H**CH_2), 5.21 (s, 2H, C**H**$_2$Ph), 4.93-5.11 (m, 4H, 2C**H**$_2$=CH), 3.37 (t, *J* = 8.5 Hz, 1H, C**H**Ph), 2.67 (ddd, *J* = 4.7, 8.8, 17.3 Hz, 1H, C**H**CH_2CH=CH_2), 1.98-2.23 (m, 2H,

C**H**$_2$CH=CH$_2$); LRMS (CI) 333.2 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{23}H_{24}O_2$) requires *m/z* 333.1854, found *m/z* 333.1854.

Benzyl Buta-2,3-dienoate: In a 500 mL round-bottomed flask, benzyl (triphenylphosphoranylidene)acetate (20.5g, 50.0 mmol) was dissolved in CH_2Cl_2 (150 mL), and Et_3N (7.0 mL, 50 mmol) in CH_2Cl_2 (50 mL) was added over 5 min. Acetyl chloride (3.6 mL, 50 mmol) in CH_2Cl_2 (50 mL) was added over 15 min. After stirring for 1h at room temperature, the solvent was removed, and the remaining yellow slurry was triturated with Et_2O (400 mL) and filtered through a pad of Celite. The filtrate was concentrated, and the residue was purified by silica gel chromatography (7% EtOAc:hexanes) to afford the title compound as a clear colorless oil in 64% yield (5.6 g, 32 mmol.) IR (thin film) 3068, 3034, 2992, 2956, 2893, 1970, 1941, 1720, 1259, 1155, 1082 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.38 (m, 5H, Ar**H**), 5.69 (dt, *J* = 1.1, 6.6 Hz, 1H, C**H**CO_2), 5.25 (s, 1H, C**H**$_2$), 5.23 (s, 1H, C**H**$_2$), 5.20 (s, 2H, C**H**$_2$Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 216.0, 165.7, 136.0, 128.7, 128.4, 128.3, 88.1, 79.8, 77.8, 76.9, 66.9; LRMS (CI) 173.1 $(M-H)^+$; HRMS (CI) exact mass calc d for ($C_{11}H_9O_2$) $[M-H]^+$ requires *m/z* 173.0603, found *m/z* 173.0605.

Benzyl Penta-2,3-dienoate: Prepared according to the procedure given for the preparation of benzyl buta-2,3-dienoate from benzyl (triphenylphosphoranylidene)acetate (13.0 g, 31.7 mmol), propionyl chloride (2.8 mL, 31.7 mmol), and Et_3N (4.4 mL, 31.7 mmol) to provide, after silica gel chromatography, the title compound as a clear, colorless oil in 43% yield (2.6 g, 13.7 mmol). IR (thin film) 3066, 3034, 2981, 2956, 2928, 1964,

1721, 1498, 1456, 1411, 1372, 1285, 1258, 1152, 1002 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.38 (m, 5H, Ar**H**), 5.58-5.65 (m, 2H, C**H**=C=C**H**), 5.19 (s, 2H, C**H**$_2$Ph), 1.77-1.81 (m, 3H, C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.3, 166.1, 136.2, 128.8, 128.7, 128.4, 128.3, 90.7, 87.8, 66.7, 13.2; LRMS (CI) 189.1 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{12}H_{11}O_2$) $(M-H)^+$ requires *m/z* 187.0759, found *m/z* 187.0752.

Benzyl 5-Methylhexa-2,3-dienoate: Prepared according to the procedure given for the preparation of benzyl buta-2,3-dienoate from benzyl (triphenylphosphoranylidene)acetate (13.0 g, 31.7 mmol), isovaleryl chloride (3.9 mL, 31.7 mmol), and Et_3N (4.4 mL, 31.7 mmol) to provide, after silica gel chromatography, the title compound as a clear colorless oil in 50% yield (3.5 g, 16.0 mmol). IR (thin film) 3034, 2963, 2872, 1958, 1722, 1498, 1456, 1414, 1383, 1320, 1251, 1150, 1003 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.37 (m, 5H, Ar**H**), 5.63-5.69 (m, 2H, **H**C=C=C**H**), 5.22 (d, *J* = 12.6 Hz, 1H, C**H**$_2$), 5.14 (d, *J* = 12.6 Hz, 1H, C**H**$_2$), 2.42-2.54 (m, 1H, C**H**$(CH_3)_2$), 1.08 (d, *J* = 7.1 Hz, 6H, $(CH_3)_2$); ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.7, 166.2, 136.3, 128.7, 128.3, 128.2, 102.9, 89.4, 66.7, 28.1, 22.7, 22.6; LRMS (CI) 217.1 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{14}H_{17}O_2$) requires *m/z* 217.1228, found *m/z* 217.1235.

Benzyl 2,3,6-heptatrienoate: Prepared according to the procedure given for the preparation of benzyl buta-2,3-dienoate from benzyl (triphenylphosphoranylidene)acetate (13.0 g, 31.7 mmol), 4-pentenoyl chloride (3.5 mL, 31.7 mmol), and Et_3N (4.4 mL, 31.7 mmol) to provide, after silica gel chromatography, the title compound as a clear colorless oil in 76% yield (5.1 g, 24.0 mmol). IR (thin film) 3034, 1961, 1721, 1640, 1498, 1456,

1419, 1374, 1259, 1151, 996 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.38 (m, 5H, Ar**H**), 5.79-5.92 (m, 1H, CH_2=C**H**), 5.62-5.70 (m, 2H, C**H**=C=C**H**), 5.07-5.25 (m, 4H, C$\mathbf{H}_2$Ph and C$\mathbf{H}_2$=CH), 2.87-2.93 (m, 2H, CHC$\mathbf{H}_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.9, 165.9, 136.2, 134.9, 128.7, 128.4, 128.3, 116.8, 94.0, 88.8, 66.8, 32.0; LRMS (CI) 215.1 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{14}H_{15}O_2$) requires *m/z* 215.1072, found *m/z* 215.1066.

Benzyl 4-Chlorobuta-2,3-dienoate: Prepared according to the procedure given for the preparation of benzyl buta-2,3-dienoate from benzyl (triphenylphosphoranylidene)acetate (5.0 g, 12.2 mmol), chloroacetyl chloride (1.0 mL, 12.2 mmol), and Et_3N (1.7 mL, 12.2 mmol). The crude residue was purified by silica gel chromatography (10% EtOAc:hexanes) to provide the title compound as a clear colorless oil in 32% yield (0.8 g, 4.0 mmol). IR (thin film) 3053, 1719, 1456, 1388, 1361, 1262, 1162 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.40 (m, 5H, Ar**H**), 6.47 (d, *J* = 5.9 Hz, 1H, C**H**CO_2), 6.00 (d, *J* = 5.9 Hz, 1H, C**H**Cl), 5.25 (d, *J* = 12.6 Hz, 1H, C$\mathbf{H}_2$Ph), 5.20 (d, *J* = 12.3 Hz, 1H, C$\mathbf{H}_2$Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.7, 163.3, 135.6, 128.8, 128.7, 128.5, 95.9, 93.3, 67.5. LRMS (CI) 209.3 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{11}H_{10}ClO_2$) requires *m/z* 209.0369, found *m/z* 209.0366.

Benzyl 4-Phthalimidobuta-2,3-dienoate: Prepared according to the procedure given for the preparation of benzyl buta-2,3-dienoate from benzyl (triphenylphosphoranylidene)acetate (10.0 g, 24.4 mmol), phthalylglycyl chloride (5.5 g,

24.4 mmol), and Et_3N (3.4 mL, 24.4 mmol). The crude residue was purified by silica gel chromatography (35% EtOAc:hexanes) to provide the title compound as a yellow oil in 20% yield (1.6 g, 5.0 mmol). The compound was unstable and was used immediately after purification. IR (thin film) 3030, 2955, 1784, 1725, 1437, 1380, 1261, 1209, 1157 cm^{-1};[1]H NMR (300 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 3.3, 5.5 Hz, 2H, NPhth**H**), 7.73 (dd, *J* = 3.3, 5.5 Hz, 2H, NPhth**H**), 7.29-7.38 (m, 6H, Ar**H** and C**H**CO_2), 6.30 (d, *J* = 6.0 Hz, 1H, C**H**CN), 5.24 (d, *J* = 12.6 Hz, 1H, C**H**$_2$Ph), 5.19 (d, *J* = 12.6 Hz, 1H, C**H**$_2$Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.4, 164.9, 164.1, 135.8, 134.9, 132.0, 128.7, 128.5, 128.4, 124.0, 97.2, 92.2, 67.3.

(*E*)-3-Methyl Cinnamyl Pyrrolidine: (*E*)-3-phenyl-2-buten-1-ol was prepared using a modification of the procedure outlined by Corey and coworkers:[4] To a solution of copper(I)iodide (2.9 g, 15.4 mmol) and methyl lithium (23.0 mL of 1.3 M solution in Et_2O, 29.9 mmol) in Et_2O (10 mL) at 0 °C was added a solution of 3-iodo-3-phenyl-2-propen-1-ol (1.0 g, 3.8 mmol) in Et_2O (3 mL). The reaction mixture was stirred at 0 °C for 87 h and then washed with sat. aq. NH_4Cl (200 mL), dried (Na_2SO_4), and concentrated. The crude residue was purified by silica gel chromatography to provide (*E*)-3-phenyl-2-buten-1-ol in 69% yield (390 mg, 2.6 mmol). Spectroscopic data of this material were in complete agreement with reported literature values[5].

The allyl pyrrolidine was prepared using a modification of the procedure outlined by Froyen and coworkers.[6] To a solution of 3-phenyl-2-buten-1-ol (280 mg, 1.9 mmol) and PPh_3 (0.51 g, 1.9 mmol) in THF (3 mL) at 0 °C was added N-bromosuccinimide

[4] Corey, E. J.; Chen, H. K. *Tetrahedron Lett.*, **1973**, *18*, 1611.

(0.35 g, 1.9 mmol) portionwise. After 15 min pyrrolidine (0.32 mL, 3.9 mL) was added at the reaction mixture was allowed to warm to room temperature. After 30 min 1N HCl (3 mL) was added and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 2 mL) and then basified to pH = 10 with 1N NaOH (4 mL). The aqueous layer was extracted with Et_2O (3 x 2 mL) and the combined organic extracts were dried (Na_2SO_4) and concentrated. The crude residue was purified by silica gel chromatography to provide the title compound as a yellow oil in 53% yield (208 mg, 1.0 mmol). IR (thin film) 3082, 3057, 3030, 2966, 2874, 2780, 1599, 1494, 1458, 1445, 1376, 1348, 1315, 1290, 1276, 1242, 1200, 1140 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23-7.43 (m, 5H, Ar**H**), 5.97 (t, *J* = 7.4 Hz, 1H, C=C**H**), 3.30 (d, *J* = 6.6 Hz, 2H, CHC**H**$_2$), 2.56-2.61 (m, 4H, N(C**H**$_2$CH$_2$)$_2$), 2.08 (s, 3H, C**H**$_3$), 1.79-1.83 (m, 4H, N(CH$_2$C**H**$_2$)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 136.4, 128.4, 127.0, 125.9, 125.9, 54.5, 54.5, 23.9, 16.6; LRMS (CI) 201.2 $(M)^+$; HRMS (CI) exact mass calc d for ($C_{14}H_{18}N$) $(M-H)^+$ requires *m/z* 200.1439, found *m/z* 200.1431.

Geranyl Pyrrolidine: Prepared from geraniol (4.3 mL, 25.0 mmol) according to the procedure outlined for the preparation of (*E*)-3-methyl cinnamyl pyrrolidine to provide the title compound as a yellow oil in 23% yield (1.2 g, 5.7 mmol). IR (thin film) 2967, 2927, 2778, 1445, 1377, 1348, 1140 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$) δ 5.24 (t, *J* = 7.1, 1H, C**H**CH$_2$N), 5.01 (t, *J* = 6.0 Hz, 1H, (CH$_3$)$_2$C=C**H**), 2.99 (d, *J* = 7.1 Hz, 2H, CHC**H**$_2$N), 2.40-2.42 (m, 4H, N(C**H**$_2$CH$_2$)$_2$), 1.89-2.02 (m, 4H, CHC**H**$_2$C**H**$_2$), 1.69-1.71 (m, 4H, N(CH$_2$C**H**$_2$)$_2$), 1.59 (s, 3H, C**H**$_3$), 1.56 (s, 3H, C**H**$_3$), 1.51 (s, 3H, C**H**$_3$); ^{13}C NMR

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[5] Bussas, R.; M nsterer, H.; Kresze, G. *J. Org. Chem.*, **1983**, *48*, 2828.
[6] Froyen P.; Juvvik, P. *Tetrahedron Lett.* **1995**, *36*, 9555.

(75 MHz, $CDCl_3$) δ 137.4, 131.4, 124.3, 122.0, 54.2, 53.6, 40.0, 26.7, 26.0 23.7, 18.0, 16.6; LRMS (CI) 208.2 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{14}H_{26}N$) requires *m/z* 208.2065, found *m/z* 208.2060.

Neryl Pyrrolidine: Prepared from nerol (4.5 mL, 25.0 mmol) according to the procedure outlined for the preparation of (*E*)-3-methyl cinnamyl pyrrolidine to provide the title compound as a yellow oil in 24% yield (1.3 g, 6.0 mmol). IR (thin film) 2966, 2928, 2778, 1447, 1377, 1344, 1140 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$) δ 5.19-5.25 (m, 1H, C**H**CH_2N), 5.00-5.04 (m, 1H, $(CH_3)_2C$=C**H**), 2.97 (d, *J* = 7.1 Hz, 2H, CHC**H**$_2$N), 2.38-2.42 (m, 4H, N(C**H**$_2CH_2)_2$), 1.97 (brs, 4H, N(CH_2C**H**$_2)_2$), 1.65-1.70 (m, 4H, CHC**H**$_2$C**H**$_2$), 1.62 (s, 3H, C**H**$_3$), 1.58 (s, 3H, C**H**$_3$), 1.51 (s, 3H, C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4, 131.6, 124.2, 123.0, 54.3, 53.5, 32.4, 26.8, 26.0, 23.8, 23.7, 17.9; LRMS (CI) 208.2 $(MH)^+$; HRMS (CI) exact mass calc d for ($C_{14}H_{26}N$) requires *m/z* 208.2065, found *m/z* 208.2061.

Table 1. Crystal data and structure refinement for THL01 (CCDC 189664).

Empirical formula	$C_{19}H_{25}NO_2$
Formula weight	299.40
Crystallization Solvent	Hexanes
Crystal Habit	Block
Crystal size	0.24 x 0.20 x 0.19 mm^3
Crystal color	Colorless

Data Collection

Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	98(2) K
θ range for 11109 reflections used in lattice determination	2.50 to 28.00°
Unit cell dimensions	a = 8.2333(6) Å b = 7.7870(6) Å β= 98.3330(10)° c = 26.445(2) Å
Volume	1677.6(2) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	$P2_1/n$
Density (calculated)	1.185 Mg/m^3
F(000)	648
Data collection program	Bruker SMART v5.054
θ range for data collection	1.56 to 28.44°
Completeness to θ = 28.44°	93.2 %
Index ranges	$-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-34 \leq l \leq 35$
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	27787
Independent reflections	3936 [R_{int}= 0.0526]
Absorption coefficient	0.076 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9857 and 0.9820

Table 1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	3936 / 0 / 299
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.978
Final R indices [$I>2\sigma(I)$, 3020 reflections]	R1 = 0.0412, *w*R2 = 0.0638
R indices (all data)	R1 = 0.0567, *w*R2 = 0.0651
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	0.245 and -0.250 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Methyl (2*E*,4*R,5*R**)-4-Phenyl-5-methyl-3-pyrrolidinohepta-2,6-dienoate**

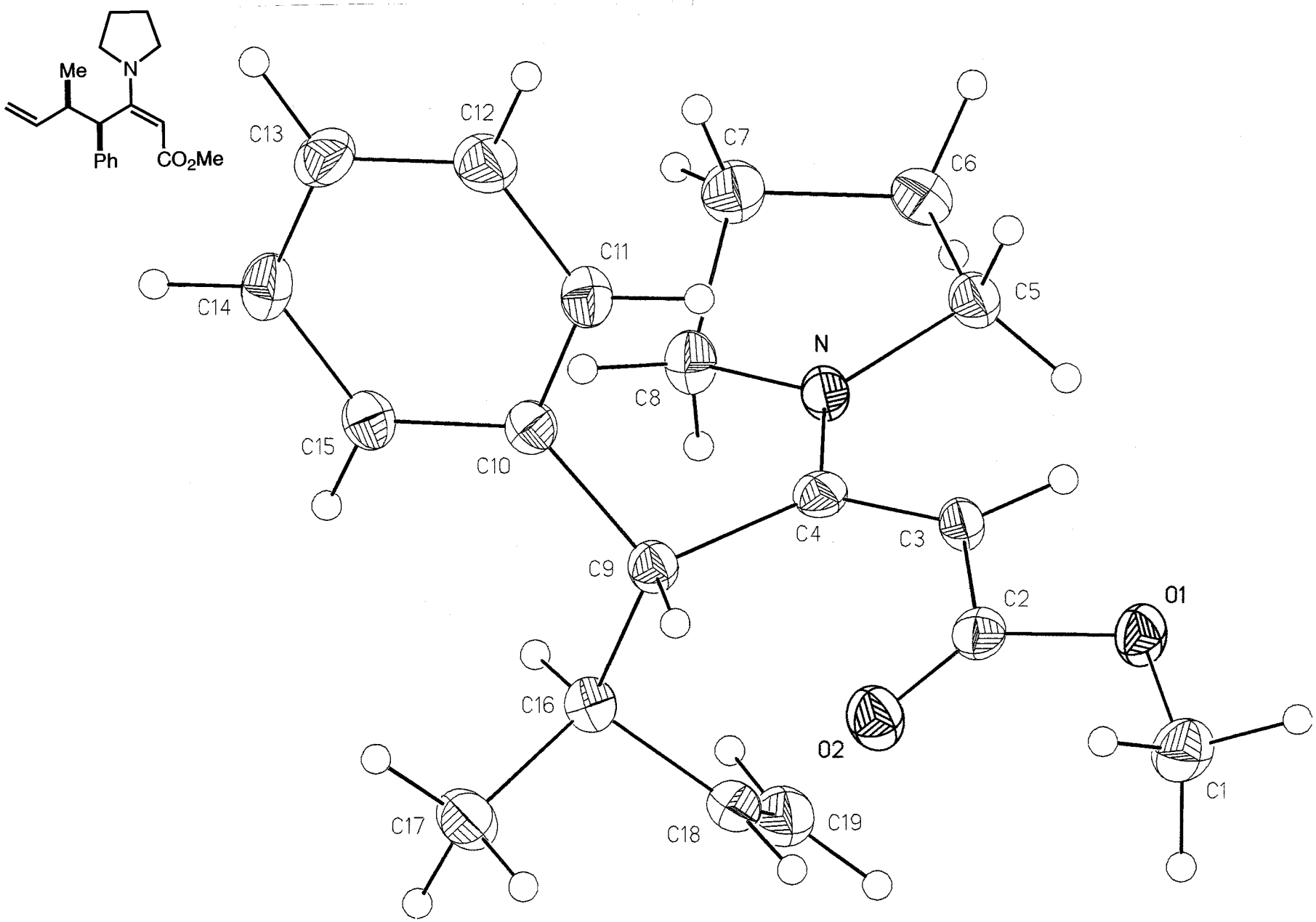


Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for THL01 (CCDC 189664). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1)	3163(1)	5676(1)	99(1)	23(1)
O(2)	1695(1)	5536(1)	751(1)	26(1)
N	3983(1)	10583(1)	1079(1)	19(1)
C(1)	2387(2)	4111(2)	-95(1)	27(1)
C(2)	2668(1)	6321(1)	530(1)	20(1)
C(3)	3445(1)	7955(1)	645(1)	18(1)
C(4)	3213(1)	9053(1)	1033(1)	18(1)
C(5)	5198(1)	11092(2)	753(1)	21(1)
C(6)	5808(2)	12845(2)	955(1)	25(1)
C(7)	5362(2)	12903(2)	1492(1)	27(1)
C(8)	3739(2)	11981(2)	1433(1)	23(1)
C(9)	2149(1)	8565(2)	1435(1)	18(1)
C(10)	3191(1)	8541(1)	1963(1)	19(1)
C(11)	4710(1)	7726(2)	2013(1)	23(1)
C(12)	5750(2)	7700(2)	2473(1)	27(1)
C(13)	5282(2)	8496(2)	2897(1)	27(1)
C(14)	3773(2)	9296(2)	2857(1)	24(1)
C(15)	2736(2)	9319(1)	2394(1)	21(1)
C(16)	510(1)	9571(2)	1385(1)	21(1)
C(17)	-768(2)	8578(2)	1634(1)	28(1)
C(18)	-141(1)	9885(2)	833(1)	22(1)
C(19)	-325(1)	11386(2)	609(1)	28(1)

Table 3. Bond lengths [Å] and angles [°] for THL01 (CCDC 189664).

O(1)-C(2)	1.3612(12)	C(4)-N-C(8)	127.36(9)
O(1)-C(1)	1.4362(14)	C(5)-N-C(8)	110.05(8)
O(2)-C(2)	1.2207(12)	O(1)-C(1)-H(1A)	110.7(7)
N-C(4)	1.3467(13)	O(1)-C(1)-H(1B)	105.4(7)
N-C(5)	1.4664(13)	H(1A)-C(1)-H(1B)	111.5(9)
N-C(8)	1.4686(13)	O(1)-C(1)-H(1C)	110.1(6)
C(1)-H(1A)	0.990(12)	H(1A)-C(1)-H(1C)	109.3(9)
C(1)-H(1B)	0.997(13)	H(1B)-C(1)-H(1C)	109.7(9)
C(1)-H(1C)	1.000(12)	O(2)-C(2)-O(1)	120.83(10)
C(2)-C(3)	1.4370(15)	O(2)-C(2)-C(3)	130.18(10)
C(3)-C(4)	1.3707(14)	O(1)-C(2)-C(3)	108.98(9)
C(3)-H(3)	0.935(10)	C(4)-C(3)-C(2)	127.20(10)
C(4)-C(9)	1.5188(14)	C(4)-C(3)-H(3)	119.9(6)
C(5)-C(6)	1.5241(16)	C(2)-C(3)-H(3)	112.6(6)
C(5)-H(5A)	0.992(10)	N-C(4)-C(3)	120.30(10)
C(5)-H(5B)	0.995(11)	N-C(4)-C(9)	118.05(9)
C(6)-C(7)	1.5171(17)	C(3)-C(4)-C(9)	121.61(10)
C(6)-H(6A)	1.001(11)	N-C(5)-C(6)	104.73(9)
C(6)-H(6B)	0.987(12)	N-C(5)-H(5A)	109.8(6)
C(7)-C(8)	1.5052(16)	C(6)-C(5)-H(5A)	112.4(6)
C(7)-H(7A)	1.006(12)	N-C(5)-H(5B)	108.1(6)
C(7)-H(7B)	1.004(12)	C(6)-C(5)-H(5B)	112.4(6)
C(8)-H(8A)	0.971(10)	H(5A)-C(5)-H(5B)	109.3(9)
C(8)-H(8B)	1.012(11)	C(7)-C(6)-C(5)	104.03(10)
C(9)-C(10)	1.5302(14)	C(7)-C(6)-H(6A)	109.1(6)
C(9)-C(16)	1.5493(15)	C(5)-C(6)-H(6A)	109.8(6)
C(9)-H(9)	0.966(10)	C(7)-C(6)-H(6B)	112.4(7)
C(10)-C(15)	1.3897(15)	C(5)-C(6)-H(6B)	111.9(6)
C(10)-C(11)	1.3916(15)	H(6A)-C(6)-H(6B)	109.5(9)
C(11)-C(12)	1.3833(16)	C(8)-C(7)-C(6)	102.80(10)
C(11)-H(11)	0.966(11)	C(8)-C(7)-H(7A)	107.5(7)
C(12)-C(13)	1.3837(16)	C(6)-C(7)-H(7A)	110.6(7)
C(12)-H(12)	0.958(11)	C(8)-C(7)-H(7B)	111.9(7)
C(13)-C(14)	1.3800(16)	C(6)-C(7)-H(7B)	114.0(6)
C(13)-H(13)	0.978(11)	H(7A)-C(7)-H(7B)	109.7(9)
C(14)-C(15)	1.3873(15)	N-C(8)-C(7)	102.57(9)
C(14)-H(14)	0.973(11)	N-C(8)-H(8A)	110.8(6)
C(15)-H(15)	0.960(10)	C(7)-C(8)-H(8A)	113.8(6)
C(16)-C(18)	1.5022(15)	N-C(8)-H(8B)	108.8(6)
C(16)-C(17)	1.5303(16)	C(7)-C(8)-H(8B)	110.2(6)
C(16)-H(16)	0.996(10)	H(8A)-C(8)-H(8B)	110.3(8)
C(17)-H(17A)	1.007(12)	C(4)-C(9)-C(10)	109.71(9)
C(17)-H(17B)	0.987(13)	C(4)-C(9)-C(16)	113.44(9)
C(17)-H(17C)	1.011(11)	C(10)-C(9)-C(16)	116.70(9)
C(18)-C(19)	1.3095(16)	C(4)-C(9)-H(9)	104.5(6)
C(18)-H(18)	0.971(11)	C(10)-C(9)-H(9)	106.8(6)
C(19)-H(19A)	1.021(12)	C(16)-C(9)-H(9)	104.6(6)
C(19)-H(19B)	0.969(12)	C(15)-C(10)-C(11)	117.82(10)
		C(15)-C(10)-C(9)	124.17(10)
C(2)-O(1)-C(1)	116.11(9)	C(11)-C(10)-C(9)	118.00(10)
C(4)-N-C(5)	122.57(9)	C(12)-C(11)-C(10)	121.53(11)

C(12)-C(11)-H(11)	119.0(7)	C(17)-C(16)-C(9)	110.66(9)
C(10)-C(11)-H(11)	119.5(7)	C(18)-C(16)-H(16)	107.3(6)
C(11)-C(12)-C(13)	119.82(12)	C(17)-C(16)-H(16)	109.0(6)
C(11)-C(12)-H(12)	119.8(7)	C(9)-C(16)-H(16)	110.1(6)
C(13)-C(12)-H(12)	120.4(7)	C(16)-C(17)-H(17A)	111.2(7)
C(14)-C(13)-C(12)	119.53(11)	C(16)-C(17)-H(17B)	113.4(7)
C(14)-C(13)-H(13)	120.7(6)	H(17A)-C(17)-H(17B)	108.7(10)
C(12)-C(13)-H(13)	119.8(6)	C(16)-C(17)-H(17C)	111.3(6)
C(13)-C(14)-C(15)	120.39(11)	H(17A)-C(17)-H(17C)	106.0(9)
C(13)-C(14)-H(14)	119.9(6)	H(17B)-C(17)-H(17C)	105.9(9)
C(15)-C(14)-H(14)	119.7(6)	C(19)-C(18)-C(16)	125.92(12)
C(14)-C(15)-C(10)	120.90(11)	C(19)-C(18)-H(18)	119.1(6)
C(14)-C(15)-H(15)	118.4(6)	C(16)-C(18)-H(18)	114.9(6)
C(10)-C(15)-H(15)	120.7(6)	C(18)-C(19)-H(19A)	123.0(7)
C(18)-C(16)-C(17)	109.30(10)	C(18)-C(19)-H(19B)	121.2(7)
C(18)-C(16)-C(9)	110.36(9)	H(19A)-C(19)-H(19B)	115.8(10)

Table 4. Anisotropic displacement parameters ($Å^2 x 10^4$) for THL01 (CCDC 189664). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	271(4)	223(4)	203(4)	-58(3)	63(3)	-9(4)
O(2)	279(5)	249(5)	263(4)	-24(4)	88(4)	-44(4)
N	201(5)	203(5)	174(5)	-13(4)	58(4)	-14(4)
C(1)	292(7)	240(7)	261(7)	-68(6)	30(6)	-7(6)
C(2)	178(6)	228(6)	175(6)	14(5)	2(5)	55(5)
C(3)	178(6)	226(6)	157(6)	13(5)	51(5)	8(5)
C(4)	150(6)	205(6)	174(6)	33(5)	-6(4)	20(5)
C(5)	202(6)	238(7)	199(6)	19(5)	54(5)	-1(5)
C(6)	212(7)	256(7)	280(7)	8(6)	58(5)	-30(6)
C(7)	294(7)	243(7)	273(7)	-38(6)	44(6)	-46(6)
C(8)	276(7)	215(7)	208(6)	-15(5)	73(5)	-9(5)
C(9)	191(6)	182(6)	181(6)	-4(5)	42(5)	-14(5)
C(10)	207(6)	172(6)	182(6)	28(5)	37(5)	-31(5)
C(11)	249(7)	245(7)	192(6)	14(5)	59(5)	6(5)
C(12)	219(7)	333(7)	260(7)	61(6)	26(5)	28(6)
C(13)	282(7)	317(7)	186(6)	42(5)	-16(5)	-50(6)
C(14)	330(7)	222(7)	179(6)	-2(5)	67(5)	-37(6)
C(15)	230(6)	207(6)	211(6)	22(5)	57(5)	1(5)
C(16)	200(6)	224(7)	196(6)	-9(5)	44(5)	4(5)
C(17)	221(7)	342(8)	282(7)	36(6)	73(6)	3(6)
C(18)	168(6)	282(7)	222(6)	-30(5)	36(5)	-1(5)
C(19)	226(7)	354(8)	253(7)	36(6)	33(6)	41(6)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for THL01 (CCDC 189664).

	x	y	z	U_{iso}
H(1A)	2384(14)	3257(15)	183(5)	36(4)
H(1B)	3039(14)	3701(15)	-361(5)	39(4)
H(1C)	1231(15)	4343(14)	-254(4)	30(3)
H(3)	4093(12)	8293(13)	400(4)	17(3)
H(5A)	4675(12)	11137(12)	391(4)	18(3)
H(5B)	6086(13)	10214(14)	791(4)	23(3)
H(6A)	5198(13)	13772(14)	745(4)	29(3)
H(6B)	6997(15)	12984(14)	952(4)	29(3)
H(7A)	6163(15)	12210(15)	1733(5)	39(4)
H(7B)	5280(13)	14096(16)	1630(4)	31(3)
H(8A)	3459(12)	11528(12)	1752(4)	14(3)
H(8B)	2835(13)	12759(13)	1265(4)	23(3)
H(9)	1828(12)	7391(13)	1354(4)	14(3)
H(11)	5062(13)	7187(13)	1718(4)	26(3)
H(12)	6777(14)	7106(14)	2499(4)	27(3)
H(13)	6024(13)	8492(13)	3221(4)	25(3)
H(14)	3436(12)	9854(13)	3154(4)	20(3)
H(15)	1714(13)	9925(13)	2375(4)	18(3)
H(16)	689(12)	10714(13)	1553(4)	14(3)
H(17A)	-1801(15)	9272(15)	1634(4)	36(3)
H(17B)	-367(14)	8215(15)	1988(5)	38(4)
H(17C)	-1111(13)	7490(14)	1439(4)	27(3)
H(18)	-451(12)	8857(14)	634(4)	24(3)
H(19A)	6(14)	12512(16)	794(5)	39(4)
H(19B)	-758(14)	11488(14)	249(5)	32(3)

Table 1. Crystal data and structure refinement for THL03 (CCDC 189743).

Empirical formula	$C_{23}H_{27}NO_2$
Formula weight	349.46
Crystallization Solvent	Ethylacetate/hexanes
Crystal Habit	Lozenge
Crystal size	0.30 x 0.22 x 0.15 mm^3
Crystal color	Colorless

Data Collection

Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	98(2) K
θ range for 8464 reflections used in lattice determination	2.48 to 27.86°
Unit cell dimensions	a = 8.3194(7) Å b = 10.7382(9) Å β= 101.2320(10)° c = 11.0105(9) Å
Volume	964.79(14) $Å^3$
Z	2
Crystal system	Monoclinic
Space group	$P2_1$
Density (calculated)	1.203 Mg/m^3
F(000)	376
Data collection program	Bruker SMART v5.054
θ range for data collection	1.89 to 27.96°
Completeness to θ = 27.96°	95.1 %
Index ranges	$-10 \leq h \leq 10$, $-13 \leq k \leq 13$, $-14 \leq l \leq 14$
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	13823
Independent reflections	4301 [R_{int}= 0.0437]
Absorption coefficient	0.076 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9887 and 0.9776

Table 1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	4301 / 1 / 343
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.699
Final R indices [$I>2\sigma(I)$, 3911 reflections]	R1 = 0.0361, *w*R2 = 0.0653
R indices (all data)	R1 = 0.0413, *w*R2 = 0.0662
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Absolute structure parameter	-0.4(8)
Largest diff. peak and hole	0.236 and -0.229 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Benzyl (2*E*,4*R,5*S**)-3-Dimethylamino-4-methyl-5-phenylhepta-2,6-dienoate**

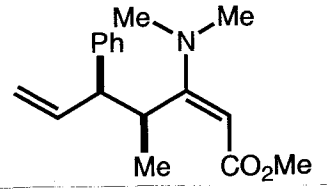


Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for THL03 (CCDC 189743). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1)	5689(1)	7542(1)	7882(1)	26(1)
O(2)	3584(1)	8078(1)	6354(1)	23(1)
N(1)	2346(1)	4378(1)	8084(1)	23(1)
C(1)	4388(2)	9244(1)	6221(2)	22(1)
C(2)	3108(2)	10214(1)	5774(1)	20(1)
C(3)	1687(2)	10287(2)	6256(1)	23(1)
C(4)	533(2)	11210(2)	5858(2)	27(1)
C(5)	792(2)	12068(1)	4978(1)	27(1)
C(6)	2213(2)	12012(2)	4509(1)	27(1)
C(7)	3361(2)	11085(1)	4901(1)	23(1)
C(8)	4347(2)	7283(1)	7267(1)	20(1)
C(9)	3304(2)	6219(1)	7309(1)	19(1)
C(10)	3542(2)	5239(1)	8131(1)	19(1)
C(11)	2449(2)	3224(2)	8792(2)	27(1)
C(12)	824(2)	4507(2)	7177(2)	26(1)
C(13)	5096(2)	5172(2)	9134(1)	21(1)
C(14)	4774(2)	5298(2)	10444(1)	24(1)
C(15)	6252(2)	4079(1)	8992(1)	22(1)
C(16)	7879(2)	4225(1)	9886(1)	19(1)
C(17)	8470(2)	3263(1)	10693(1)	21(1)
C(18)	9974(2)	3346(1)	11494(1)	24(1)
C(19)	10897(2)	4410(2)	11519(1)	25(1)
C(20)	10320(2)	5393(2)	10738(1)	25(1)
C(21)	8830(2)	5297(2)	9919(1)	23(1)
C(22)	6535(2)	3955(2)	7685(1)	25(1)
C(23)	6301(2)	2945(2)	7017(2)	37(1)

Table 3. Bond lengths [Å] and angles [°] for THL03 (CCDC 189743).

O(1)-C(8)	1.2190(17)	C(22)-H(22)	0.993(19)
O(2)-C(8)	1.3770(16)	C(23)-H(23A)	1.034(19)
O(2)-C(1)	1.4402(17)	C(23)-H(23B)	0.992(17)
N(1)-C(10)	1.3517(18)		
N(1)-C(11)	1.457(2)	C(8)-O(2)-C(1)	117.15(11)
N(1)-C(12)	1.4589(18)	C(10)-N(1)-C(11)	126.51(12)
C(1)-C(2)	1.502(2)	C(10)-N(1)-C(12)	119.72(12)
C(1)-H(1A)	0.983(14)	C(11)-N(1)-C(12)	113.54(12)
C(1)-H(1B)	0.979(14)	O(2)-C(1)-C(2)	108.81(11)
C(2)-C(3)	1.390(2)	O(2)-C(1)-H(1A)	109.2(9)
C(2)-C(7)	1.387(2)	C(2)-C(1)-H(1A)	111.2(8)
C(3)-C(4)	1.390(2)	O(2)-C(1)-H(1B)	108.4(8)
C(3)-H(3)	0.962(14)	C(2)-C(1)-H(1B)	110.9(8)
C(4)-C(5)	1.384(2)	H(1A)-C(1)-H(1B)	108.3(11)
C(4)-H(4)	0.971(16)	C(3)-C(2)-C(7)	118.84(13)
C(5)-C(6)	1.380(2)	C(3)-C(2)-C(1)	121.04(13)
C(5)-H(5)	0.952(17)	C(7)-C(2)-C(1)	120.08(13)
C(6)-C(7)	1.389(2)	C(2)-C(3)-C(4)	120.39(14)
C(6)-H(6)	0.980(16)	C(2)-C(3)-H(3)	119.9(8)
C(7)-H(7)	0.959(15)	C(4)-C(3)-H(3)	119.7(8)
C(8)-C(9)	1.441(2)	C(3)-C(4)-C(5)	120.25(15)
C(9)-C(10)	1.377(2)	C(3)-C(4)-H(4)	118.8(10)
C(9)-H(9)	0.978(14)	C(5)-C(4)-H(4)	121.0(10)
C(10)-C(13)	1.5295(19)	C(6)-C(5)-C(4)	119.66(15)
C(11)-H(11A)	0.993(18)	C(6)-C(5)-H(5)	120.6(10)
C(11)-H(11B)	0.975(18)	C(4)-C(5)-H(5)	119.7(10)
C(11)-H(11C)	0.967(16)	C(5)-C(6)-C(7)	120.13(15)
C(12)-H(12A)	0.934(16)	C(5)-C(6)-H(6)	120.2(9)
C(12)-H(12B)	0.984(19)	C(7)-C(6)-H(6)	119.7(9)
C(12)-H(12C)	0.982(16)	C(2)-C(7)-C(6)	120.72(15)
C(13)-C(14)	1.524(2)	C(2)-C(7)-H(7)	116.3(9)
C(13)-C(15)	1.545(2)	C(6)-C(7)-H(7)	123.0(9)
C(13)-H(13)	1.013(15)	O(1)-C(8)-O(2)	120.38(13)
C(14)-H(14A)	0.983(17)	O(1)-C(8)-C(9)	130.96(13)
C(14)-H(14B)	1.025(14)	O(2)-C(8)-C(9)	108.66(12)
C(14)-H(14C)	1.008(19)	C(10)-C(9)-C(8)	128.03(13)
C(15)-C(16)	1.5188(19)	C(10)-C(9)-H(9)	118.3(9)
C(15)-C(22)	1.509(2)	C(8)-C(9)-H(9)	113.5(9)
C(15)-H(15)	1.019(14)	N(1)-C(10)-C(9)	119.14(12)
C(16)-C(17)	1.389(2)	N(1)-C(10)-C(13)	120.51(13)
C(16)-C(21)	1.393(2)	C(9)-C(10)-C(13)	120.25(13)
C(17)-C(18)	1.386(2)	N(1)-C(11)-H(11A)	108.9(10)
C(17)-H(17)	0.946(17)	N(1)-C(11)-H(11B)	110.0(11)
C(18)-C(19)	1.374(2)	H(11A)-C(11)-H(11B)	103.1(14)
C(18)-H(18)	0.945(17)	N(1)-C(11)-H(11C)	112.7(10)
C(19)-C(20)	1.386(2)	H(11A)-C(11)-H(11C)	111.9(14)
C(19)-H(19)	0.982(17)	H(11B)-C(11)-H(11C)	109.8(14)
C(20)-C(21)	1.387(2)	N(1)-C(12)-H(12A)	111.0(9)
C(20)-H(20)	0.924(17)	N(1)-C(12)-H(12B)	108.7(10)
C(21)-H(21)	0.978(16)	H(12A)-C(12)-H(12B)	106.0(13)
C(22)-C(23)	1.304(2)	N(1)-C(12)-H(12C)	110.2(9)

H(12A)-C(12)-H(12C)	111.1(13)	C(21)-C(16)-C(15)	122.17(13)
H(12B)-C(12)-H(12C)	109.8(14)	C(18)-C(17)-C(16)	121.46(14)
C(10)-C(13)-C(14)	113.55(12)	C(18)-C(17)-H(17)	119.7(9)
C(10)-C(13)-C(15)	114.72(12)	C(16)-C(17)-H(17)	118.8(9)
C(14)-C(13)-C(15)	113.01(13)	C(19)-C(18)-C(17)	119.87(14)
C(10)-C(13)-H(13)	102.3(8)	C(19)-C(18)-H(18)	122.8(9)
C(14)-C(13)-H(13)	106.9(8)	C(17)-C(18)-H(18)	117.3(9)
C(15)-C(13)-H(13)	105.1(8)	C(18)-C(19)-C(20)	119.73(14)
C(13)-C(14)-H(14A)	111.9(9)	C(18)-C(19)-H(19)	121.6(10)
C(13)-C(14)-H(14B)	110.9(7)	C(20)-C(19)-H(19)	118.7(10)
H(14A)-C(14)-H(14B)	108.8(12)	C(19)-C(20)-C(21)	120.29(15)
C(13)-C(14)-H(14C)	113.3(10)	C(19)-C(20)-H(20)	122.0(10)
H(14A)-C(14)-H(14C)	102.0(13)	C(21)-C(20)-H(20)	117.7(10)
H(14B)-C(14)-H(14C)	109.6(12)	C(20)-C(21)-C(16)	120.60(14)
C(16)-C(15)-C(22)	110.01(12)	C(20)-C(21)-H(21)	116.9(9)
C(16)-C(15)-C(13)	110.49(12)	C(16)-C(21)-H(21)	122.5(9)
C(22)-C(15)-C(13)	112.28(12)	C(23)-C(22)-C(15)	125.27(17)
C(16)-C(15)-H(15)	107.4(7)	C(23)-C(22)-H(22)	120.6(11)
C(22)-C(15)-H(15)	109.1(8)	C(15)-C(22)-H(22)	113.8(11)
C(13)-C(15)-H(15)	107.3(8)	C(22)-C(23)-H(23A)	122.0(10)
C(17)-C(16)-C(21)	118.02(13)	C(22)-C(23)-H(23B)	123.3(10)
C(17)-C(16)-C(15)	119.81(13)	H(23A)-C(23)-H(23B)	114.6(14)

Table 4. Anisotropic displacement parameters ($Å^2 x 10^4$) for THL03 (CCDC 189743). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	185(5)	252(6)	316(6)	63(5)	-36(5)	-31(5)
O(2)	236(5)	178(5)	234(5)	40(4)	-23(4)	-23(4)
N(1)	201(6)	202(7)	265(7)	43(5)	23(5)	-4(6)
C(1)	225(8)	199(8)	224(8)	31(6)	23(7)	-29(6)
C(2)	203(8)	188(7)	191(7)	-28(6)	-11(6)	-36(6)
C(3)	278(8)	202(8)	212(8)	32(7)	46(6)	-16(7)
C(4)	252(8)	285(9)	285(9)	-42(7)	50(7)	7(7)
C(5)	289(9)	187(8)	286(8)	-26(7)	-93(7)	40(7)
C(6)	314(9)	222(8)	221(8)	41(7)	-46(7)	-57(7)
C(7)	216(8)	241(8)	207(8)	17(7)	1(6)	-38(7)
C(8)	214(8)	181(8)	193(7)	-6(6)	41(6)	45(6)
C(9)	159(7)	204(7)	193(8)	3(6)	-12(6)	16(6)
C(10)	184(7)	188(7)	212(7)	-21(7)	42(6)	25(6)
C(11)	278(9)	223(9)	287(9)	45(7)	19(8)	-22(7)
C(12)	213(8)	223(9)	318(10)	35(8)	-21(7)	-28(7)
C(13)	195(8)	218(8)	224(8)	11(7)	31(6)	-6(7)
C(14)	222(8)	237(8)	252(8)	-42(7)	-6(7)	30(8)
C(15)	198(8)	206(8)	256(8)	4(6)	18(6)	-5(6)
C(16)	167(7)	225(8)	194(8)	-41(6)	47(6)	29(6)
C(17)	257(8)	164(8)	236(8)	-12(6)	92(6)	3(7)
C(18)	278(9)	259(9)	202(8)	47(7)	65(7)	82(7)
C(19)	171(8)	352(10)	221(8)	1(7)	11(6)	56(7)
C(20)	200(8)	254(9)	300(8)	11(7)	49(6)	-37(7)
C(21)	206(8)	220(8)	251(8)	41(7)	30(6)	45(7)
C(22)	200(8)	309(9)	243(8)	26(7)	22(7)	81(7)
C(23)	417(10)	415(11)	275(9)	-37(9)	54(8)	12(9)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for THL03 (CCDC 189743).

	x	y	z	U_{iso}
H(1A)	5132(17)	9138(13)	5635(13)	16(4)
H(1B)	5044(16)	9474(13)	7027(13)	15(4)
H(3)	1496(17)	9693(13)	6867(13)	17(4)
H(4)	-440(20)	11252(15)	6223(13)	33(5)
H(5)	0(20)	12698(16)	4710(14)	29(4)
H(6)	2406(18)	12616(16)	3886(14)	29(4)
H(7)	4352(18)	11000(14)	4587(13)	24(4)
H(9)	2270(17)	6260(13)	6709(13)	16(4)
H(11A)	2510(20)	2513(17)	8227(16)	38(5)
H(11B)	1420(20)	3076(17)	9067(16)	44(5)
H(11C)	3349(19)	3222(16)	9496(15)	30(4)
H(12A)	290(18)	5249(16)	7295(13)	23(4)
H(12B)	80(20)	3832(18)	7308(16)	45(5)
H(12C)	1045(18)	4456(14)	6333(15)	26(4)
H(13)	5709(16)	5947(14)	8964(12)	19(4)
H(14A)	3946(19)	5938(16)	10498(14)	30(4)
H(14B)	5831(17)	5515(13)	11057(12)	14(3)
H(14C)	4260(20)	4532(18)	10739(16)	43(5)
H(15)	5717(16)	3285(13)	9229(12)	13(3)
H(17)	7804(19)	2553(16)	10715(14)	27(4)
H(18)	10310(18)	2656(15)	12014(15)	26(4)
H(19)	11960(20)	4498(16)	12084(15)	38(5)
H(20)	10880(19)	6139(16)	10764(14)	30(4)
H(21)	8494(17)	6009(15)	9376(13)	24(4)
H(22)	7040(20)	4700(18)	7384(16)	53(6)
H(23A)	5850(20)	2138(18)	7335(16)	45(5)
H(23B)	6497(19)	2894(16)	6158(16)	41(5)

Table 1. Crystal data and structure refinement for THL02 (CCDC 189742).

Empirical formula	$C_{24}H_{27}NO_2$
Formula weight	361.47
Crystallization Solvent	Hexanes/ether
Crystal Habit	Block
Crystal size	0.24 x 0.22 x 0.20 mm^3
Crystal color	Colorless

Data Collection

Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	98(2) K
θ range for 13362 reflections used in lattice determination	2.23 to 28.84°
Unit cell dimensions	a = 10.4779(7) Å b = 10.6838(7) Å c = 17.4395(11) Å
Volume	1952.2(2) $Å^3$
Z	4
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Density (calculated)	1.230 Mg/m^3
F(000)	776
Data collection program	Bruker SMART v5.054
θ range for data collection	2.24 to 28.35°
Completeness to θ = 28.35°	96.2 %
Index ranges	$-13 \le h \le 13$, $-13 \le k \le 14$, $-22 \le l \le 22$
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	28772
Independent reflections	4606 [R_{int}= 0.0534]
Absorption coefficient	0.077 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9847 and 0.9817

Table 1 (cont.)

Structure solution and Refinement

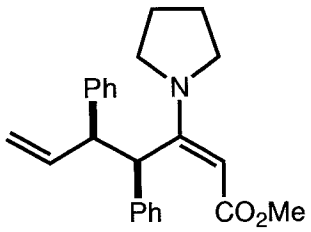
Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	4606 / 0 / 352
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.629
Final R indices [$I>2\sigma(I)$, 3972 reflections]	R1 = 0.0358, *w*R2 = 0.0532
R indices (all data)	R1 = 0.0444, *w*R2 = 0.0541
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Absolute structure parameter	-0.5(8)
Largest diff. peak and hole	0.200 and -0.238 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Methyl (2*E*,4*R,5*R**)-4,5-Diphenyl-3-pyrrolidinohepta-2,6-dienoate**



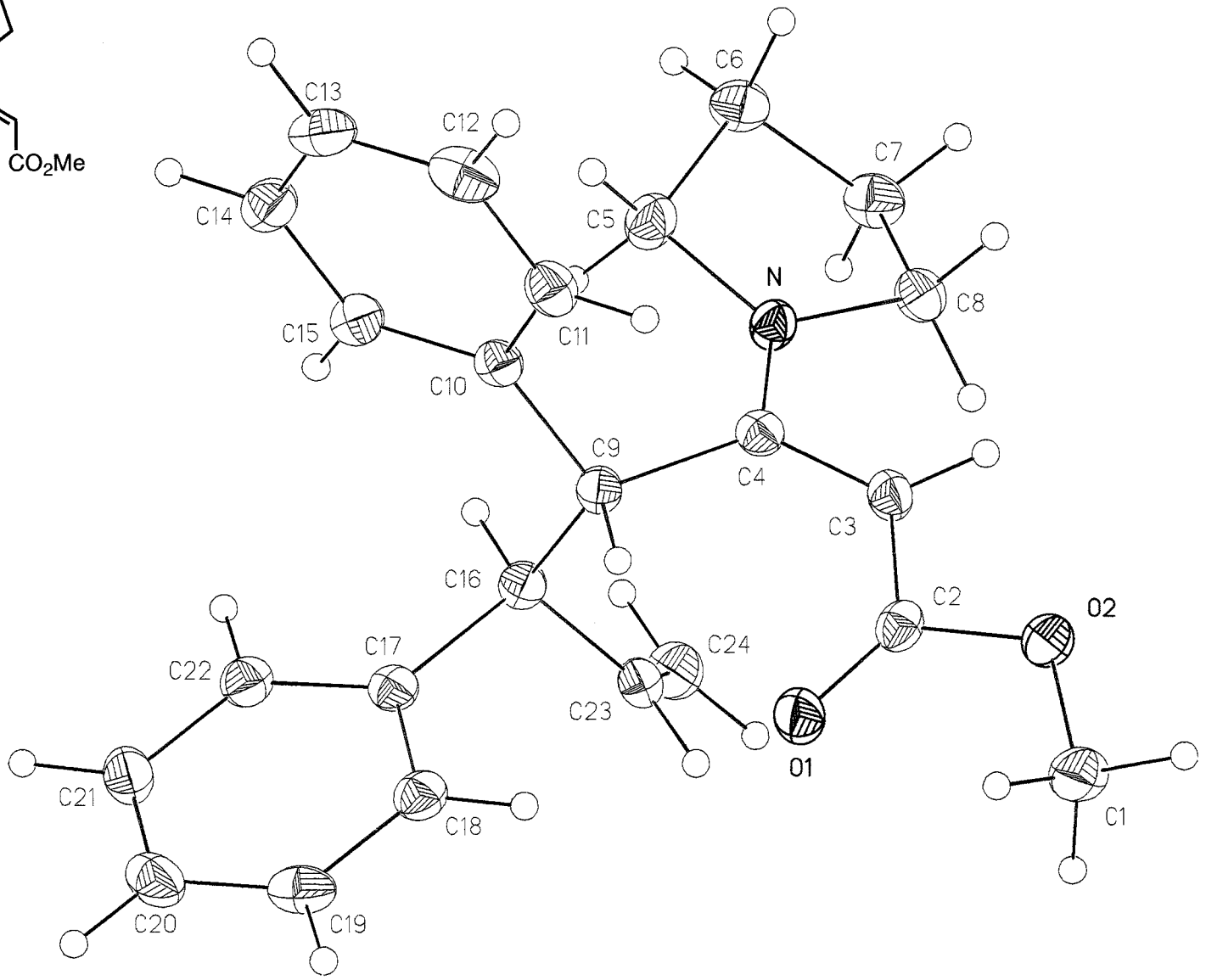


Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for THL02 (CCDC 189742). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1)	2744(1)	6191(1)	1802(1)	25(1)
O(2)	1295(1)	5324(1)	2593(1)	24(1)
N	1801(1)	9515(1)	3160(1)	19(1)
C(1)	1596(2)	4132(1)	2257(1)	28(1)
C(2)	1983(1)	6314(1)	2328(1)	19(1)
C(3)	1656(1)	7415(1)	2764(1)	19(1)
C(4)	2045(1)	8622(1)	2633(1)	17(1)
C(5)	1889(1)	10889(1)	3061(1)	24(1)
C(6)	1259(1)	11398(1)	3781(1)	23(1)
C(7)	1556(2)	10406(1)	4380(1)	24(1)
C(8)	1372(1)	9197(1)	3940(1)	22(1)
C(9)	2813(1)	8965(1)	1919(1)	17(1)
C(10)	2147(1)	9924(1)	1408(1)	18(1)
C(11)	956(1)	9626(1)	1112(1)	23(1)
C(12)	311(1)	10445(2)	631(1)	28(1)
C(13)	849(1)	11584(1)	444(1)	27(1)
C(14)	2029(1)	11898(1)	736(1)	25(1)
C(15)	2674(1)	11071(1)	1214(1)	21(1)
C(16)	4227(1)	9273(1)	2127(1)	18(1)
C(17)	5093(1)	9162(1)	1429(1)	18(1)
C(18)	5152(1)	8053(1)	1004(1)	22(1)
C(19)	5954(1)	7964(1)	374(1)	25(1)
C(20)	6710(1)	8963(1)	154(1)	28(1)
C(21)	6673(1)	10055(1)	578(1)	27(1)
C(22)	5879(1)	10148(1)	1215(1)	22(1)
C(23)	4696(1)	8421(1)	2754(1)	20(1)
C(24)	5094(1)	8803(2)	3427(1)	26(1)

Table 3. Bond lengths [Å] and angles [°] for THL02 (CCDC 189742).

O(1)-C(2)	1.2220(14)	C(22)-H(22)	0.968(12)
O(2)-C(2)	1.3613(14)	C(23)-C(24)	1.3099(18)
O(2)-C(1)	1.4365(16)	C(23)-H(23)	1.026(13)
N-C(4)	1.3487(15)	C(24)-H(24A)	0.980(14)
N-C(8)	1.4717(15)	C(24)-H(24B)	1.004(14)
N-C(5)	1.4805(16)		
C(1)-H(1A)	1.032(14)	C(2)-O(2)-C(1)	115.71(10)
C(1)-H(1B)	0.996(13)	C(4)-N-C(8)	121.58(10)
C(1)-H(1C)	0.990(16)	C(4)-N-C(5)	127.58(10)
C(2)-C(3)	1.4419(18)	C(8)-N-C(5)	110.84(10)
C(3)-C(4)	1.3718(18)	O(2)-C(1)-H(1A)	110.9(8)
C(3)-H(3)	0.938(11)	O(2)-C(1)-H(1B)	104.0(7)
C(4)-C(9)	1.5278(16)	H(1A)-C(1)-H(1B)	113.3(11)
C(5)-C(6)	1.5196(18)	O(2)-C(1)-H(1C)	109.8(9)
C(5)-H(5A)	1.003(13)	H(1A)-C(1)-H(1C)	106.9(12)
C(5)-H(5B)	0.998(13)	H(1B)-C(1)-H(1C)	111.9(11)
C(6)-C(7)	1.5202(19)	O(1)-C(2)-O(2)	121.11(11)
C(6)-H(6A)	0.971(12)	O(1)-C(2)-C(3)	129.68(12)
C(6)-H(6B)	0.991(12)	O(2)-C(2)-C(3)	109.21(10)
C(7)-C(8)	1.5148(19)	C(4)-C(3)-C(2)	127.50(12)
C(7)-H(7A)	0.975(13)	C(4)-C(3)-H(3)	117.5(7)
C(7)-H(7B)	0.968(14)	C(2)-C(3)-H(3)	114.9(7)
C(8)-H(8A)	1.018(12)	N-C(4)-C(3)	119.70(11)
C(8)-H(8B)	1.020(12)	N-C(4)-C(9)	119.08(11)
C(9)-C(10)	1.5262(16)	C(3)-C(4)-C(9)	121.14(11)
C(9)-C(16)	1.5597(17)	N-C(5)-C(6)	103.37(11)
C(9)-H(9)	0.975(12)	N-C(5)-H(5A)	110.7(7)
C(10)-C(15)	1.3860(17)	C(6)-C(5)-H(5A)	113.7(7)
C(10)-C(11)	1.3880(17)	N-C(5)-H(5B)	111.1(7)
C(11)-C(12)	1.3880(19)	C(6)-C(5)-H(5B)	109.9(7)
C(11)-H(11)	0.920(12)	H(5A)-C(5)-H(5B)	108.0(11)
C(12)-C(13)	1.380(2)	C(7)-C(6)-C(5)	103.28(11)
C(12)-H(12)	0.969(15)	C(7)-C(6)-H(6A)	115.2(7)
C(13)-C(14)	1.378(2)	C(5)-C(6)-H(6A)	111.1(7)
C(13)-H(13)	0.972(14)	C(7)-C(6)-H(6B)	108.2(7)
C(14)-C(15)	1.3906(17)	C(5)-C(6)-H(6B)	109.4(7)
C(14)-H(14)	0.989(13)	H(6A)-C(6)-H(6B)	109.4(10)
C(15)-H(15)	0.970(13)	C(6)-C(7)-C(8)	102.72(11)
C(16)-C(23)	1.5064(17)	C(6)-C(7)-H(7A)	113.2(7)
C(16)-C(17)	1.5228(17)	C(8)-C(7)-H(7A)	114.3(8)
C(16)-H(16)	1.027(11)	C(6)-C(7)-H(7B)	109.2(8)
C(17)-C(22)	1.3881(17)	C(8)-C(7)-H(7B)	110.7(8)
C(17)-C(18)	1.3991(17)	H(7A)-C(7)-H(7B)	106.8(10)
C(18)-C(19)	1.3862(18)	N-C(8)-C(7)	103.47(11)
C(18)-H(18)	0.988(13)	N-C(8)-H(8A)	109.3(7)
C(19)-C(20)	1.383(2)	C(7)-C(8)-H(8A)	113.9(7)
C(19)-H(19)	0.962(13)	N-C(8)-H(8B)	110.6(7)
C(20)-C(21)	1.383(2)	C(7)-C(8)-H(8B)	112.3(7)
C(20)-H(20)	0.963(13)	H(8A)-C(8)-H(8B)	107.2(10)
C(21)-C(22)	1.3908(18)	C(4)-C(9)-C(10)	113.31(10)
C(21)-H(21)	1.003(13)	C(4)-C(9)-C(16)	111.17(10)

C(10)-C(9)-C(16)	115.35(10)	C(17)-C(16)-H(16)	107.7(6)
C(4)-C(9)-H(9)	104.6(7)	C(9)-C(16)-H(16)	110.0(6)
C(10)-C(9)-H(9)	103.9(7)	C(22)-C(17)-C(18)	118.31(12)
C(16)-C(9)-H(9)	107.5(7)	C(22)-C(17)-C(16)	120.62(11)
C(15)-C(10)-C(11)	118.01(12)	C(18)-C(17)-C(16)	121.03(11)
C(15)-C(10)-C(9)	123.65(11)	C(19)-C(18)-C(17)	120.32(13)
C(11)-C(10)-C(9)	118.34(11)	C(19)-C(18)-H(18)	119.5(7)
C(12)-C(11)-C(10)	121.25(14)	C(17)-C(18)-H(18)	120.1(7)
C(12)-C(11)-H(11)	121.0(8)	C(18)-C(19)-C(20)	120.92(13)
C(10)-C(11)-H(11)	117.8(8)	C(18)-C(19)-H(19)	118.3(7)
C(13)-C(12)-C(11)	119.94(14)	C(20)-C(19)-H(19)	120.8(7)
C(13)-C(12)-H(12)	121.5(8)	C(21)-C(20)-C(19)	119.11(13)
C(11)-C(12)-H(12)	118.6(8)	C(21)-C(20)-H(20)	120.9(9)
C(14)-C(13)-C(12)	119.63(14)	C(19)-C(20)-H(20)	120.0(8)
C(14)-C(13)-H(13)	120.3(8)	C(20)-C(21)-C(22)	120.32(14)
C(12)-C(13)-H(13)	120.0(8)	C(20)-C(21)-H(21)	121.2(7)
C(13)-C(14)-C(15)	120.17(14)	C(22)-C(21)-H(21)	118.4(7)
C(13)-C(14)-H(14)	118.7(7)	C(17)-C(22)-C(21)	120.98(13)
C(15)-C(14)-H(14)	121.2(7)	C(17)-C(22)-H(22)	120.5(7)
C(10)-C(15)-C(14)	121.00(13)	C(21)-C(22)-H(22)	118.5(7)
C(10)-C(15)-H(15)	121.1(7)	C(24)-C(23)-C(16)	124.51(13)
C(14)-C(15)-H(15)	117.9(7)	C(24)-C(23)-H(23)	120.0(7)
C(23)-C(16)-C(17)	109.83(10)	C(16)-C(23)-H(23)	115.5(7)
C(23)-C(16)-C(9)	110.58(10)	C(23)-C(24)-H(24A)	119.7(8)
C(17)-C(16)-C(9)	111.35(10)	C(23)-C(24)-H(24B)	123.7(8)
C(23)-C(16)-H(16)	107.3(6)	H(24A)-C(24)-H(24B)	116.7(11)

Table 4. Anisotropic displacement parameters ($Å^2 x 10^4$) for THL02 (CCDC 189742). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	298(5)	205(5)	253(5)	-14(4)	76(4)	-7(4)
O(2)	249(5)	156(5)	311(5)	-19(4)	41(4)	-22(4)
N	230(6)	161(6)	173(5)	-2(5)	16(5)	-3(5)
C(1)	250(8)	169(8)	413(9)	-38(7)	30(7)	-26(7)
C(2)	191(7)	182(7)	199(6)	28(6)	-36(6)	-12(6)
C(3)	209(7)	201(7)	170(7)	8(5)	36(6)	-8(6)
C(4)	155(6)	204(7)	163(6)	6(5)	-19(5)	14(5)
C(5)	307(9)	177(7)	234(7)	-5(6)	35(7)	-6(6)
C(6)	242(8)	220(8)	234(7)	-55(6)	0(6)	16(7)
C(7)	261(8)	274(8)	197(7)	-42(6)	-7(6)	28(7)
C(8)	242(8)	243(8)	172(7)	-8(6)	30(6)	10(6)
C(9)	200(7)	157(6)	158(6)	-14(5)	17(6)	-7(5)
C(10)	211(7)	196(7)	123(6)	-24(5)	17(5)	25(6)
C(11)	225(7)	249(8)	203(7)	-25(6)	25(6)	-15(7)
C(12)	220(8)	392(9)	239(7)	-75(7)	-34(6)	49(7)
C(13)	317(8)	299(8)	185(7)	-20(6)	-21(6)	134(7)
C(14)	335(9)	213(7)	191(7)	-5(6)	21(6)	50(7)
C(15)	234(8)	216(7)	189(7)	-7(6)	-10(6)	13(6)
C(16)	203(7)	167(7)	160(6)	-12(5)	5(5)	0(6)
C(17)	169(7)	219(7)	151(6)	18(5)	-26(5)	32(6)
C(18)	213(8)	224(7)	214(7)	26(6)	-25(6)	34(6)
C(19)	259(8)	298(8)	205(7)	-48(6)	-42(6)	100(7)
C(20)	236(8)	411(9)	198(7)	48(7)	32(6)	85(7)
C(21)	223(7)	312(9)	264(7)	74(6)	29(6)	6(7)
C(22)	226(7)	214(8)	221(7)	13(6)	-3(6)	25(6)
C(23)	186(7)	223(7)	201(7)	33(6)	39(6)	6(6)
C(24)	258(8)	302(9)	221(7)	29(6)	-9(6)	23(7)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for THL02 (CCDC 189742).

	x	y	z	U_{iso}
H(1A)	1629(14)	4195(12)	1667(8)	38(4)
H(1B)	909(12)	3568(12)	2447(7)	25(4)
H(1C)	2451(15)	3856(14)	2429(9)	51(5)
H(3)	1156(11)	7265(11)	3200(6)	14(3)
H(5A)	1460(12)	11158(12)	2574(7)	26(4)
H(5B)	2797(12)	11167(12)	3039(7)	26(4)
H(6A)	1570(12)	12233(12)	3900(7)	21(4)
H(6B)	322(12)	11425(11)	3706(6)	13(3)
H(7A)	1029(12)	10477(12)	4839(7)	26(3)
H(7B)	2434(13)	10494(12)	4544(7)	29(4)
H(8A)	1903(12)	8471(11)	4142(6)	20(3)
H(8B)	444(12)	8912(11)	3935(7)	17(3)
H(9)	2817(12)	8203(11)	1611(7)	20(3)
H(11)	615(12)	8859(12)	1236(7)	17(3)
H(12)	-529(14)	10210(13)	447(8)	43(4)
H(13)	398(13)	12158(12)	108(8)	31(4)
H(14)	2393(12)	12725(12)	606(6)	22(4)
H(15)	3496(12)	11330(11)	1415(6)	15(3)
H(16)	4294(10)	10174(11)	2327(6)	8(3)
H(18)	4632(12)	7323(12)	1156(7)	22(4)
H(19)	5958(12)	7195(12)	86(7)	20(3)
H(20)	7242(13)	8896(13)	-294(8)	37(4)
H(21)	7189(12)	10806(12)	427(7)	26(4)
H(22)	5857(12)	10931(12)	1494(7)	22(3)
H(23)	4691(11)	7483(13)	2626(7)	25(4)
H(24A)	5087(12)	9698(13)	3548(7)	29(4)
H(24B)	5390(13)	8223(13)	3844(8)	35(4)

Table 1. Crystal data and structure refinement for THL04 (CCDC 192895).

Empirical formula	$C_{32}H_{30}N_2O_4$
Formula weight	506.58
Crystallization Solvent	Dichloromethane/hexanes
Crystal Habit	Fragment
Crystal size	0.26 x 0.19 x 0.18 mm^3
Crystal color	Pale yellow

Data Collection

Preliminary Photos	Rotation	
Type of diffractometer	Bruker SMART 1000	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	98(2) K	
θ range for 10881 reflections used in lattice determination	2.26 to 27.92°	
Unit cell dimensions	a = 9.1446(7) Å	α= 92.6790(10)°
	b = 10.8456(8) Å	β= 91.5470(10)°
	c = 13.1962(10) Å	γ = 99.8700(10)°
Volume	1287.19(17) $Å^3$	
Z	2	
Crystal system	Triclinic	
Space group	P-1	
Density (calculated)	1.307 Mg/m^3	
F(000)	536	
Data collection program	Bruker SMART v5.054	
θ range for data collection	1.55 to 28.17°	
Completeness to θ = 28.17°	92.5 %	
Index ranges	$-12 \leq h \leq 12$, $-14 \leq k \leq 14$, $-16 \leq l \leq 17$	
Data collection scan type	ω scans at 7 ϕ settings	
Data reduction program	Bruker SAINT v6.022	
Reflections collected	26175	
Independent reflections	5848 [R_{int}= 0.0518]	
Absorption coefficient	0.086 mm^{-1}	
Absorption correction	None	

Table 1 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	5848 / 0 / 463
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.587
Final R indices [$I>2\sigma(I)$, 4420 reflections]	R1 = 0.0381, *w*R2 = 0.0628
R indices (all data)	R1 = 0.0555, *w*R2 = 0.0651
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Largest diff. peak and hole	0.252 and -0.246 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Benzyl (2*E*, 4*S,5*S**)-5-Phenyl-4-phthalimido-3-pyrrolidinohepta-2,6-dienoate**

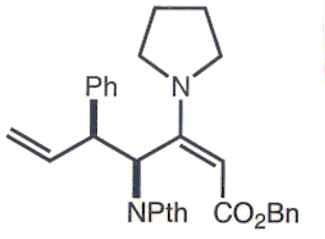


Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for THL02 (CCDC 189742). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1)	2744(1)	6191(1)	1802(1)	25(1)
O(2)	1295(1)	5324(1)	2593(1)	24(1)
N	1801(1)	9515(1)	3160(1)	19(1)
C(1)	1596(2)	4132(1)	2257(1)	28(1)
C(2)	1983(1)	6314(1)	2328(1)	19(1)
C(3)	1656(1)	7415(1)	2764(1)	19(1)
C(4)	2045(1)	8622(1)	2633(1)	17(1)
C(5)	1889(1)	10889(1)	3061(1)	24(1)
C(6)	1259(1)	11398(1)	3781(1)	23(1)
C(7)	1556(2)	10406(1)	4380(1)	24(1)
C(8)	1372(1)	9197(1)	3940(1)	22(1)
C(9)	2813(1)	8965(1)	1919(1)	17(1)
C(10)	2147(1)	9924(1)	1408(1)	18(1)
C(11)	956(1)	9626(1)	1112(1)	23(1)
C(12)	311(1)	10445(2)	631(1)	28(1)
C(13)	849(1)	11584(1)	444(1)	27(1)
C(14)	2029(1)	11898(1)	736(1)	25(1)
C(15)	2674(1)	11071(1)	1214(1)	21(1)
C(16)	4227(1)	9273(1)	2127(1)	18(1)
C(17)	5093(1)	9162(1)	1429(1)	18(1)
C(18)	5152(1)	8053(1)	1004(1)	22(1)
C(19)	5954(1)	7964(1)	374(1)	25(1)
C(20)	6710(1)	8963(1)	154(1)	28(1)
C(21)	6673(1)	10055(1)	578(1)	27(1)
C(22)	5879(1)	10148(1)	1215(1)	22(1)
C(23)	4696(1)	8421(1)	2754(1)	20(1)
C(24)	5094(1)	8803(2)	3427(1)	26(1)

Table 3. Bond lengths [Å] and angles [°] for THL02 (CCDC 189742).

O(1)-C(2)	1.2220(14)	C(22)-H(22)	0.968(12)
O(2)-C(2)	1.3613(14)	C(23)-C(24)	1.3099(18)
O(2)-C(1)	1.4365(16)	C(23)-H(23)	1.026(13)
N-C(4)	1.3487(15)	C(24)-H(24A)	0.980(14)
N-C(8)	1.4717(15)	C(24)-H(24B)	1.004(14)
N-C(5)	1.4805(16)		
C(1)-H(1A)	1.032(14)	C(2)-O(2)-C(1)	115.71(10)
C(1)-H(1B)	0.996(13)	C(4)-N-C(8)	121.58(10)
C(1)-H(1C)	0.990(16)	C(4)-N-C(5)	127.58(10)
C(2)-C(3)	1.4419(18)	C(8)-N-C(5)	110.84(10)
C(3)-C(4)	1.3718(18)	O(2)-C(1)-H(1A)	110.9(8)
C(3)-H(3)	0.938(11)	O(2)-C(1)-H(1B)	104.0(7)
C(4)-C(9)	1.5278(16)	H(1A)-C(1)-H(1B)	113.3(11)
C(5)-C(6)	1.5196(18)	O(2)-C(1)-H(1C)	109.8(9)
C(5)-H(5A)	1.003(13)	H(1A)-C(1)-H(1C)	106.9(12)
C(5)-H(5B)	0.998(13)	H(1B)-C(1)-H(1C)	111.9(11)
C(6)-C(7)	1.5202(19)	O(1)-C(2)-O(2)	121.11(11)
C(6)-H(6A)	0.971(12)	O(1)-C(2)-C(3)	129.68(12)
C(6)-H(6B)	0.991(12)	O(2)-C(2)-C(3)	109.21(10)
C(7)-C(8)	1.5148(19)	C(4)-C(3)-C(2)	127.50(12)
C(7)-H(7A)	0.975(13)	C(4)-C(3)-H(3)	117.5(7)
C(7)-H(7B)	0.968(14)	C(2)-C(3)-H(3)	114.9(7)
C(8)-H(8A)	1.018(12)	N-C(4)-C(3)	119.70(11)
C(8)-H(8B)	1.020(12)	N-C(4)-C(9)	119.08(11)
C(9)-C(10)	1.5262(16)	C(3)-C(4)-C(9)	121.14(11)
C(9)-C(16)	1.5597(17)	N-C(5)-C(6)	103.37(11)
C(9)-H(9)	0.975(12)	N-C(5)-H(5A)	110.7(7)
C(10)-C(15)	1.3860(17)	C(6)-C(5)-H(5A)	113.7(7)
C(10)-C(11)	1.3880(17)	N-C(5)-H(5B)	111.1(7)
C(11)-C(12)	1.3880(19)	C(6)-C(5)-H(5B)	109.9(7)
C(11)-H(11)	0.920(12)	H(5A)-C(5)-H(5B)	108.0(11)
C(12)-C(13)	1.380(2)	C(7)-C(6)-C(5)	103.28(11)
C(12)-H(12)	0.969(15)	C(7)-C(6)-H(6A)	115.2(7)
C(13)-C(14)	1.378(2)	C(5)-C(6)-H(6A)	111.1(7)
C(13)-H(13)	0.972(14)	C(7)-C(6)-H(6B)	108.2(7)
C(14)-C(15)	1.3906(17)	C(5)-C(6)-H(6B)	109.4(7)
C(14)-H(14)	0.989(13)	H(6A)-C(6)-H(6B)	109.4(10)
C(15)-H(15)	0.970(13)	C(6)-C(7)-C(8)	102.72(11)
C(16)-C(23)	1.5064(17)	C(6)-C(7)-H(7A)	113.2(7)
C(16)-C(17)	1.5228(17)	C(8)-C(7)-H(7A)	114.3(8)
C(16)-H(16)	1.027(11)	C(6)-C(7)-H(7B)	109.2(8)
C(17)-C(22)	1.3881(17)	C(8)-C(7)-H(7B)	110.7(8)
C(17)-C(18)	1.3991(17)	H(7A)-C(7)-H(7B)	106.8(10)
C(18)-C(19)	1.3862(18)	N-C(8)-C(7)	103.47(11)
C(18)-H(18)	0.988(13)	N-C(8)-H(8A)	109.3(7)
C(19)-C(20)	1.383(2)	C(7)-C(8)-H(8A)	113.9(7)
C(19)-H(19)	0.962(13)	N-C(8)-H(8B)	110.6(7)
C(20)-C(21)	1.383(2)	C(7)-C(8)-H(8B)	112.3(7)
C(20)-H(20)	0.963(13)	H(8A)-C(8)-H(8B)	107.2(10)
C(21)-C(22)	1.3908(18)	C(4)-C(9)-C(10)	113.31(10)
C(21)-H(21)	1.003(13)	C(4)-C(9)-C(16)	111.17(10)

O(2)-C(8)-C(7)	127.51(11)	C(22)-C(21)-H(21A)	111.1(7)
N(1)-C(8)-C(7)	105.86(10)	C(20)-C(21)-H(21A)	109.4(6)
N(1)-C(9)-C(19)	112.01(9)	C(22)-C(21)-H(21B)	113.7(7)
N(1)-C(9)-C(10)	113.77(9)	C(20)-C(21)-H(21B)	112.0(7)
C(19)-C(9)-C(10)	115.21(9)	H(21A)-C(21)-H(21B)	108.0(9)
N(1)-C(9)-H(9)	104.3(6)	C(21)-C(22)-C(23)	103.75(10)
C(19)-C(9)-H(9)	103.8(6)	C(21)-C(22)-H(22A)	112.6(7)
C(10)-C(9)-H(9)	106.5(6)	C(23)-C(22)-H(22A)	112.2(6)
C(11)-C(10)-C(13)	108.14(9)	C(21)-C(22)-H(22B)	109.7(7)
C(11)-C(10)-C(9)	110.13(10)	C(23)-C(22)-H(22B)	110.1(6)
C(13)-C(10)-C(9)	112.21(9)	H(22A)-C(22)-H(22B)	108.5(9)
C(11)-C(10)-H(10)	109.1(6)	N(2)-C(23)-C(22)	104.41(9)
C(13)-C(10)-H(10)	107.0(6)	N(2)-C(23)-H(23A)	108.9(6)
C(9)-C(10)-H(10)	110.2(6)	C(22)-C(23)-H(23A)	111.9(6)
C(12)-C(11)-C(10)	123.58(13)	N(2)-C(23)-H(23B)	108.4(6)
C(12)-C(11)-H(11)	120.1(7)	C(22)-C(23)-H(23B)	115.2(6)
C(10)-C(11)-H(11)	116.3(7)	H(23A)-C(23)-H(23B)	107.8(9)
C(11)-C(12)-H(12A)	122.5(8)	C(19)-C(24)-C(25)	127.61(11)
C(11)-C(12)-H(12B)	120.2(8)	C(19)-C(24)-H(24)	120.2(6)
H(12A)-C(12)-H(12B)	117.3(11)	C(25)-C(24)-H(24)	112.2(6)
C(14)-C(13)-C(18)	118.36(11)	O(3)-C(25)-O(4)	120.77(10)
C(14)-C(13)-C(10)	120.22(11)	O(3)-C(25)-C(24)	130.50(11)
C(18)-C(13)-C(10)	121.14(10)	O(4)-C(25)-C(24)	108.74(10)
C(15)-C(14)-C(13)	121.10(12)	O(4)-C(26)-C(27)	111.69(10)
C(15)-C(14)-H(14)	120.0(7)	O(4)-C(26)-H(26A)	110.2(7)
C(13)-C(14)-H(14)	118.9(7)	C(27)-C(26)-H(26A)	111.2(7)
C(16)-C(15)-C(14)	119.81(12)	O(4)-C(26)-H(26B)	105.9(6)
C(16)-C(15)-H(15)	121.6(7)	C(27)-C(26)-H(26B)	109.7(6)
C(14)-C(15)-H(15)	118.5(7)	H(26A)-C(26)-H(26B)	107.9(9)
C(15)-C(16)-C(17)	119.84(12)	C(32)-C(27)-C(28)	119.05(12)
C(15)-C(16)-H(16)	120.8(7)	C(32)-C(27)-C(26)	122.19(11)
C(17)-C(16)-H(16)	119.3(7)	C(28)-C(27)-C(26)	118.76(11)
C(18)-C(17)-C(16)	120.22(12)	C(29)-C(28)-C(27)	120.66(12)
C(18)-C(17)-H(17)	120.1(7)	C(29)-C(28)-H(28)	120.2(7)
C(16)-C(17)-H(17)	119.7(7)	C(27)-C(28)-H(28)	119.1(7)
C(17)-C(18)-C(13)	120.65(11)	C(30)-C(29)-C(28)	120.17(13)
C(17)-C(18)-H(18)	119.1(6)	C(30)-C(29)-H(29)	120.7(7)
C(13)-C(18)-H(18)	120.2(6)	C(28)-C(29)-H(29)	119.1(7)
N(2)-C(19)-C(24)	119.27(10)	C(29)-C(30)-C(31)	119.52(13)
N(2)-C(19)-C(9)	120.35(10)	C(29)-C(30)-H(30)	120.8(8)
C(24)-C(19)-C(9)	120.37(10)	C(31)-C(30)-H(30)	119.7(8)
N(2)-C(20)-C(21)	103.11(10)	C(32)-C(31)-C(30)	120.31(14)
N(2)-C(20)-H(20A)	110.9(6)	C(32)-C(31)-H(31)	119.0(7)
C(21)-C(20)-H(20A)	114.0(6)	C(30)-C(31)-H(31)	120.7(7)
N(2)-C(20)-H(20B)	109.0(6)	C(31)-C(32)-C(27)	120.28(12)
C(21)-C(20)-H(20B)	111.1(6)	C(31)-C(32)-H(32)	120.6(7)
H(20A)-C(20)-H(20B)	108.6(9)	C(27)-C(32)-H(32)	119.1(7)
C(22)-C(21)-C(20)	102.56(10)		

Table 4. Anisotropic displacement parameters ($Å^2 x 10^4$) for THL04 (CCDC 192895). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	236(4)	201(4)	221(4)	-11(4)	-16(4)	21(4)
O(2)	297(5)	224(5)	251(5)	-32(4)	-33(4)	16(4)
O(3)	193(4)	273(5)	234(5)	9(4)	0(4)	39(4)
O(4)	203(4)	293(5)	216(5)	-43(4)	-47(4)	38(4)
N(1)	186(5)	184(5)	175(5)	3(4)	-20(4)	31(4)
N(2)	179(5)	214(5)	188(5)	-10(4)	0(4)	39(4)
C(1)	171(6)	213(7)	184(6)	5(5)	34(5)	49(5)
C(2)	169(6)	251(7)	169(6)	18(5)	38(5)	56(5)
C(3)	251(7)	266(7)	230(7)	22(6)	31(5)	68(6)
C(4)	310(7)	331(8)	266(7)	102(6)	24(6)	134(6)
C(5)	249(7)	441(9)	200(7)	71(6)	-22(6)	95(6)
C(6)	221(7)	331(8)	197(7)	12(6)	-1(5)	27(6)
C(7)	174(6)	266(7)	169(6)	21(5)	23(5)	43(5)
C(8)	186(6)	246(7)	183(6)	-16(5)	18(5)	31(5)
C(9)	184(6)	194(6)	176(6)	13(5)	-24(5)	33(5)
C(10)	195(6)	182(6)	224(7)	2(5)	3(5)	33(5)
C(11)	255(7)	249(7)	231(7)	24(6)	55(6)	104(6)
C(12)	446(9)	311(9)	361(9)	96(7)	87(7)	163(7)
C(13)	205(6)	207(6)	199(6)	34(5)	-8(5)	81(5)
C(14)	253(7)	222(7)	272(7)	7(5)	-9(6)	49(6)
C(15)	356(8)	276(7)	225(7)	-36(6)	-1(6)	106(6)
C(16)	274(7)	348(8)	212(7)	44(6)	45(6)	126(6)
C(17)	200(7)	329(8)	223(7)	42(6)	-16(5)	52(6)
C(18)	241(7)	257(7)	172(6)	3(5)	-21(5)	66(5)
C(19)	195(6)	143(6)	221(6)	26(5)	2(5)	59(5)
C(20)	198(6)	242(7)	217(7)	-18(6)	-21(5)	29(5)
C(21)	199(7)	250(7)	278(7)	-10(6)	-13(6)	15(6)
C(22)	209(7)	240(7)	257(7)	17(6)	12(5)	39(6)
C(23)	216(7)	214(7)	205(7)	2(5)	21(5)	52(5)
C(24)	197(6)	204(6)	184(6)	5(5)	7(5)	46(5)
C(25)	244(7)	169(6)	192(6)	22(5)	-23(5)	62(5)
C(26)	194(6)	263(7)	251(7)	-31(6)	-49(5)	-1(5)
C(27)	227(6)	259(7)	147(6)	-42(5)	0(5)	36(5)
C(28)	250(7)	311(8)	182(7)	-35(6)	-20(5)	24(6)
C(29)	333(8)	410(9)	201(7)	-44(6)	-48(6)	129(7)
C(30)	561(10)	333(8)	183(7)	-10(6)	-38(6)	202(8)
C(31)	452(9)	271(8)	273(8)	-13(6)	41(7)	5(7)
C(32)	270(7)	268(7)	241(7)	-37(6)	2(6)	27(6)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for THL04 (CCDC 192895).

	x	y	z	U_{iso}
H(3)	5531(12)	3066(11)	8673(8)	23(3)
H(4)	7108(12)	3094(11)	10118(9)	29(3)
H(5)	8333(13)	4986(11)	10907(9)	34(3)
H(6)	7982(12)	6898(11)	10257(9)	27(3)
H(9)	3612(12)	6596(10)	6711(8)	18(3)
H(10)	5119(11)	9035(10)	7383(8)	15(3)
H(11)	2755(13)	8459(11)	5842(9)	32(4)
H(12A)	3601(14)	10482(12)	5344(10)	41(4)
H(12B)	4881(15)	10691(12)	6308(10)	43(4)
H(14)	4275(13)	9865(11)	8853(8)	28(3)
H(15)	2470(12)	9985(11)	10028(9)	26(3)
H(16)	176(12)	8588(10)	9901(9)	27(3)
H(17)	-282(13)	7070(11)	8546(8)	28(3)
H(18)	1530(11)	6985(10)	7309(8)	19(3)
H(20A)	7318(11)	8737(10)	7049(8)	18(3)
H(20B)	8188(12)	7552(11)	7092(8)	25(3)
H(21A)	8858(12)	9610(11)	5785(8)	26(3)
H(21B)	10040(13)	9096(10)	6493(9)	28(3)
H(22A)	9832(12)	8277(11)	4627(9)	26(3)
H(22B)	9829(12)	7263(11)	5458(8)	25(3)
H(23A)	7297(12)	7728(10)	4350(8)	22(3)
H(23B)	7542(11)	6391(11)	4710(8)	18(3)
H(24)	5162(11)	6417(9)	4369(8)	15(3)
H(26A)	601(13)	5025(11)	4087(9)	30(3)
H(26B)	1173(12)	4591(11)	3007(9)	24(3)
H(28)	-1379(13)	5744(11)	3005(9)	29(3)
H(29)	-2178(14)	7458(11)	2258(9)	33(3)
H(30)	-326(13)	9155(12)	1864(9)	35(4)
H(31)	2190(13)	9158(12)	2217(9)	33(4)
H(32)	2926(13)	7444(11)	2973(8)	28(3)